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Iron-promoted remediation of Atrazine: Solution and amended sandy column studies

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Iron-Promoted Remediation of Atrazine:

Solution and Amended Sandy Column Studies

(TITLE)

BY

Donghua Zeng

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Iron-Promoted Remediation of Atrazine:

Solution and Amended Sandy Column Studies

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Advisor

Abstract

Atrazine is a very important pre-emergent triazine herbicide. It exhibits potential carcinogenic and other toxic properties, which makes its use controversial in agriculture. In the Midwest, atrazine contamination of groundwater and surface water are commonly found in areas where it has been applied, which causes health concerns. This research project is designed to evaluate the feasibility of remediating the atrazine-polluted water by using zero valent iron (Fe^0). Iron was selected because it is cheap and nontoxic compared with other removal methods. A column packed with Fe^0 and sand was employed to study the remediation of atrazine, with the purpose of developing a possible *in situ* application of removing atrazine by Fe^0. At the experimental concentration level of 40ppm, a maximum of 63.1% of atrazine removal was observed in the column. The degradation was found to be dependent on pH. Bromide, which was used as a conservative tracer, was monitored by using XRF.

Keywords: Atrazine, zero valent iron, pH, column, remediation, Br tracer.

Dedication

I dedicate this page to my parents. Without their patience, understanding, support and most of all love, the completion of this work would not have been possible.

I also dedicate this page to my son for his understanding and willingness to stay home alone while I was working in the lab. Without his self-discipline, this completion would not have been possible.

Acknowledgements

I wish to acknowledge with thanks the significant contributions of the following people who offered numerous helpful suggestions and lab conveniences: Professor Richard L. Keiter, Professor T. Howard Black, Professor Jonathan P. Blitz, Professor Mark E. McGuire, Professor Ellen A. Keiter, Dr. Edward M. Treadwell, Mr. Kenneth R. Osborne, Mr. Xiguang Zhao and Mr. Yong Liu. I wish to acknowledge the great help and instruction of my adviser, Professor Douglas G. Klarup. Finally, I wish to express my appreciation to Professor Blitz again for his help and advice as I started my graduate study in EIU.

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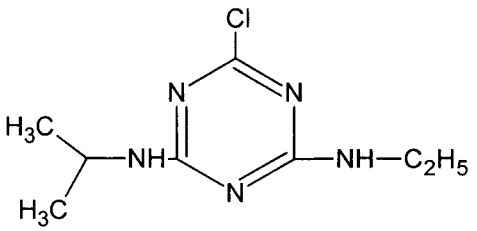
1. INTRODUCTION

Atrazine, 2-chloro-4-ethylamino-6-isoproylamino-s-triazine, is a selective preemergent triazine herbicide that inhibits the normal photosynthetic electron transport system (Chapman *et al.*, 1992; Devine *et al.*, 1993) to control broad leaf and grassy weeds in fields of corn, sorghum, sugarcane, pineapple and other crops and it has been the most widely used herbicide in the United States for the past 30 years (Boundy-Mills *et al.*, 1997).



Atrazine, $C_8H_{14}ClN_5$, 215.69

Other major triazine herbicides are Simazine, Cyanazine and Propazine. All of them contain the chloroaromatic triazine ring.

In 1994, atrazine treatment in the US was used on 67% of corn acreage, 65% of grain sorghum and 90% of sugarcane fields (Bridges, 1998). The US Environmental Protection Agency (EPA) estimated that about 55 million pounds of atrazine were used in 1992 (Lin

et al., 1995) and 60 million pounds in 1993 (Environ News, 2002). Even in 1996, it was the most common agricultural herbicide in the United States with about 73 million pounds of atrazine used (Capel *et al.*, 2001). Currently, there are no global herbicide standards for drinking water. In the U.S.A., the regulation is based on toxicological data of individual chemicals. The maximum concentration level (MCLs) for atrazine in U.S.A. is 3 μg/L (EPA, 1991).

An herbicide can transport from an agricultural field (terrestrial environment) via a surface water system in form of interflow and overland flow to marine environment eventually. The process involved in this continuum is called "field runoff" in agricultural science (Capel *et al.*, 2001). Throughout 10 Midwestern states, atrazine has been detected in 55% of watershed basins investigated, and results show concentrations exceeding the maximum contamination level of 3μ g /L (Tevera-Mendoza *et al.*, 2002; Pensabene *et al.*, 2002). Ma and Spalding (1997) reported maximum atrazine inputs to Recharge Lake in Nebraska, which occurred in May and June runoff evens with the average lake concentration level of 36 and 17μg/L in 1993 and 1994 respectively.

A field study of a Mississippi River alluvial soil in Southern Louisiana indicated that during 1995-1997, losses in runoff for atrazine were 5.2–10.8% of the applied (Southwick *et al.*, 2003). Similar studies conducted by U.S. Geological Survey (USGS) in northern Missouri and southern Iowa watersheds found that atrazine was detected in 100% of samples in 1997, 1998 and 1999, with median atrazine concentrations ranging

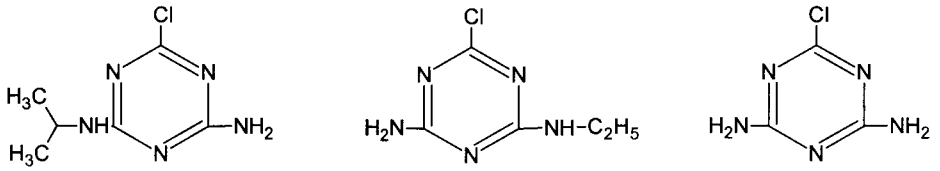
from 3.8 to 6.3 μg/L (Lerch *et al.*, 2003). Richards *et al.* (1996) reported a remarkable coincidence of loss of herbicides applied with the intense spring rainfall events during the second and third quarters in each year.

Atrazine can also be significantly lost to surface runoff and into groundwater via leaching from the regions where it has been frequently used. For example, an investigation through the National Water-Quality Assessment Program of the U.S. Geological Survey, conducted between 1992 and 1999, indicated that atrazine and its degradant, deethylatrazine were found together 284 times in 1497 domestic drinking-water wells and public supply wells (Squillance *et al.*, 2002). The concentration of atrazine runoff and groundwater depends on the soil, storm duration, proximity after atrazine application, and field site characteristics (Christopher and Bird, 1992; Douglas *et al.*, 2001). Lioyd-Smith *et al.*(1999) reported that areas of sandy soil with high infiltration rates are particularly susceptible to atrazine contamination.

The toxicity of atrazine is high for aquatic organisms (Arántegui *et al.*, 1995). For example, Christopher and Bird (1992) indicated that the overall decline of fish and wildfowl population had much to do with the increased atrazine levels in the sediments. It has been reported that the maximum contaminant level (MCL) of 3μg/L atrazine in drinking water could cause chromosomal damage in hamster ovary cells (Newman, 1995), and similar abnormalities occurred in the bone marrow of mice, which could lead to cancer and birth defects (Biradar *et al.*, 1995). It was also reported that occurrence of

atrazine with nitrate (at current MCLs) could inhibit the ability of mice to make antibodies (Pape-Lindstrom *et al.*, 1997). Tavera-Mendoza *et al.* (2002) reported a significant alteration on primary and secondary oocyte of *Xenopus laevis* tadpoles during the sexual differentiation. A study performed by endocrinologist Hayes also confirmed that ppb doses of atrazine could disrupt the sexual development of frogs while alternations of gonads occurred from 0.1 ppb (Environ. News, 2002). Recent evidence found in Florida suggested that feminization of amphibians near sugar cane fields may be linked to atrazine due to the highest usage of atrazine in sugar cane fields (Environ News, 2003). Patlack (1996) reported that chlorinated pesticides, including atrazine, triggered breast cancer development by affecting the metabolism of estradiol.

Currently, no official limit of atrazine degradants in drinking water has ever been set in the United States (Rollag *et al.*, 1996; Liu *et al.*, 1996). However, two major metabolites, deethylatrazine (DEA) and deisopropylatrzine (DIA), are structurally and toxicologically similar to atrazine (Ciba-Geigy Coporation, 1993). Their risks to ecosystems should not be ignored. Another chlorinate metabolite, didealkylatrazine (DDA) may also show toxicity (Winkelmann and Klarine, 1991). Actually, according to a 1991 investigation of the US Geological Survey (USGS) of pesticides in Midwestern groundwater, the maximum concentration level of combined atrazine compounds (atrazine + DEA + DIA) was 4.48μ g, about 50% above the atrazine MCL (Liu *et al.*, 1996).



Deethylatrazine (DEA)

Deisopropylatrazine (DIA)

Dideallkylatrazine (DDA)

FIGURE 1. Chlorinated Metabolites in Natural Environment.

Generally, herbicides losses vary significantly in different watersheds. For a given watershed, atrazine losses were dominated by " the unique combination of the natural terrestrial characteristics (soil type, slope, etc.), the agricultural practices (buffer strips, cultivation methods, etc.) and the weather (Caple *et al.*, 2001). The timing of rainfall relative to atrazine application was a critical factor that affected the year-to-year runoff (Lerch *et al.*, 2003). Clay type fields have low infiltration rates and high surface runoff and thus are vulnerable to surface transportation of agricultural chemicals (Blanchard *et al.*, 2000).

Consistent with other triazine herbicides, atrazine shows high persistence in soils, high leaching potential, slow hydrolysis, low vapour pressure, moderate solubility in water and moderate absorption into organic matter and clay (US EPA, 1990). Atrazine environmental persistence, run-off characteristics, and potential toxic and carcinogenic

effects have been a concern to agricultural and environmental communities for decades.

1.1. Natural Fate of Atrazine

It is believed (Report I, 2002) that 5 processes dominated the degradation / reduction of atrazine in the natural environment: ① hydrolysis, ② adsorption, ③ microbial degradation, ④ photodegradation, and ⑤ volatilization, and that, environmentally, chemical degradation may be more important than biodegradation (Speclab, 2003). Further study (Capel *et al.*, 2001) also indicated that volatilization plays no significant role because of it's low Henry's law constant (2.48×10^{-4} Pa · m^3 mol^{-1}). Natural photodecompostion is not significant (Evgenidou, *et al.* 2002).

The major natural chemical degradation is hydrolysis which is affected by a variety of factors such as pH, organic matter, moisture and the temperature of the soil. While at neutral pH hydrolysis of atrazine is fairly slow, it proceeds fairly quickly in both acidic and basic environment. Humic materials, like fulvic acid, can significantly catalyze the hydrolysis. Photolysis of atrazine was not observed in alcohol or water at wavelenths longer than 300 nm. However, at 290 nm, the half life of atrazine (10 mg/L) was reported as 25 hr at 15℃ (Speclab, 2003 and Report I, 2002). Table 1 shows the atrazine degradation in the presence of humic acid.

Accinelli *et al.* (2001) observed a half life 49 days of atrazine in non-sterile surface soil under aerobic conditions, and 119 days for non-sterile subsoil. In sterile soils, the

difference was not significant: 115 days and 110 days respectively. The half-lives can be much longer in similar soils but under anaerobic condition: 124 and 405 days in non-sterile surface soil and subsoil respectively. However, in sterile soil, the degradation half life can be as long as 770 days!

TABLE 1. Atrazine half life (at 25°C) in aquatic environment*

pH 4.0	no additive	244 days
pH 4.0	2% humic acid	173 days
pH 2.9	5mg/ml fulvic acid	35.8 days
pH 4.5	5mg/ml fulvic acid	174 days
pH 6.0	5mg/ml fulvic acid	398 days
pH 7.0	5mg/ml fulvic acid	742 days

* Report I and Speclab

Theoretically, atrazine in the natural environment can be metabolized via dealkylation, deamination, dechlorination and ring cleavage. It is believed that microbes oxidatively dealkylate the ethyl and isopropyl branches from the atrazine molecule and hydroxyatrazine is formed from abiotic hydrolysis (Wachett *et al.*, 1998), which occurs under acidic condition and can be catalyzed by soil organic matter. In the following scheme, dashed lines show the possible bond cleavage.

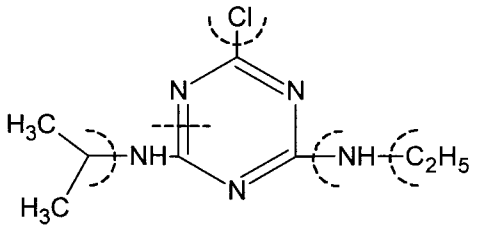


FIGURE 2. Bond cleavage during microbial metabolism (derived form the report by Wachett *et al.*,1998)

The proposed pathway is as follows (Cater, 1996), but a definitive identification of metabolic intermediates of atrazine ring cleavage is lacking.

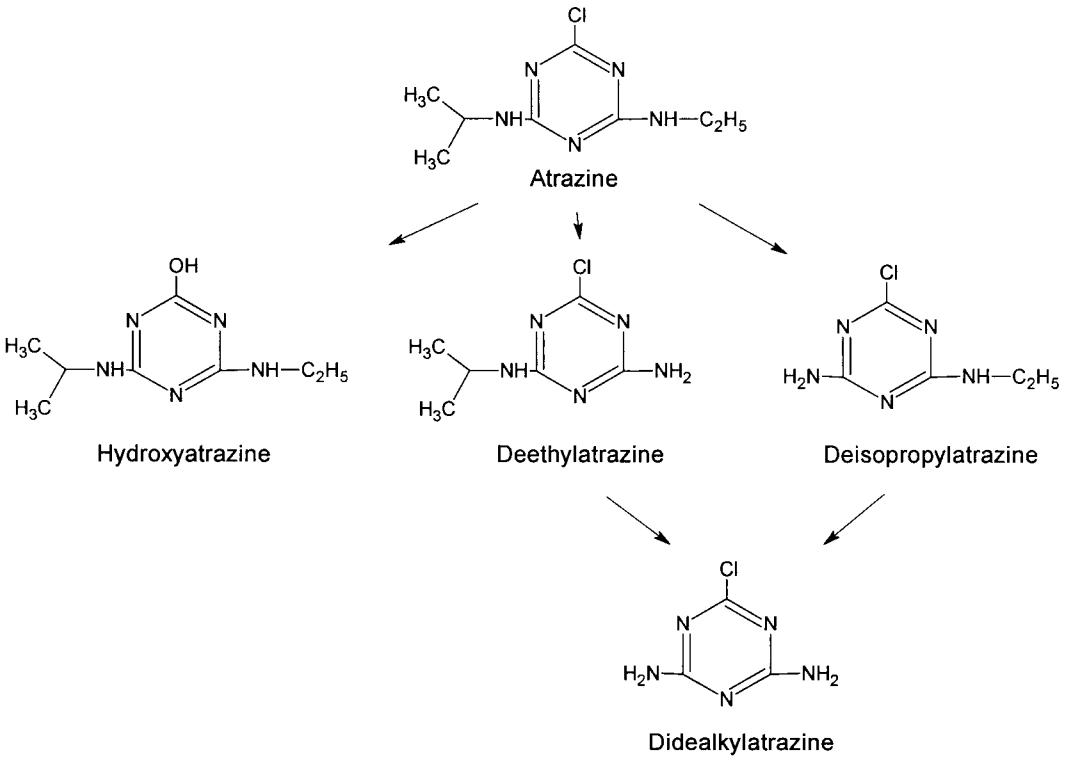


FIGURE 3. Degradation of atrazine in a natural environment. Dealkylation is the major mechanism involved in the microbial degradation process.

Recently, The University of Minnesota Biocatalysis/Biodegradation Database (Report II, 2002) highlighted a metapathway for atrazine degradation. A number of different enzymes have been identified that are capable of metabolizing atrazine with the final products as ammonia and carbon dioxide. The detailed pathways are shown in Figure 4.

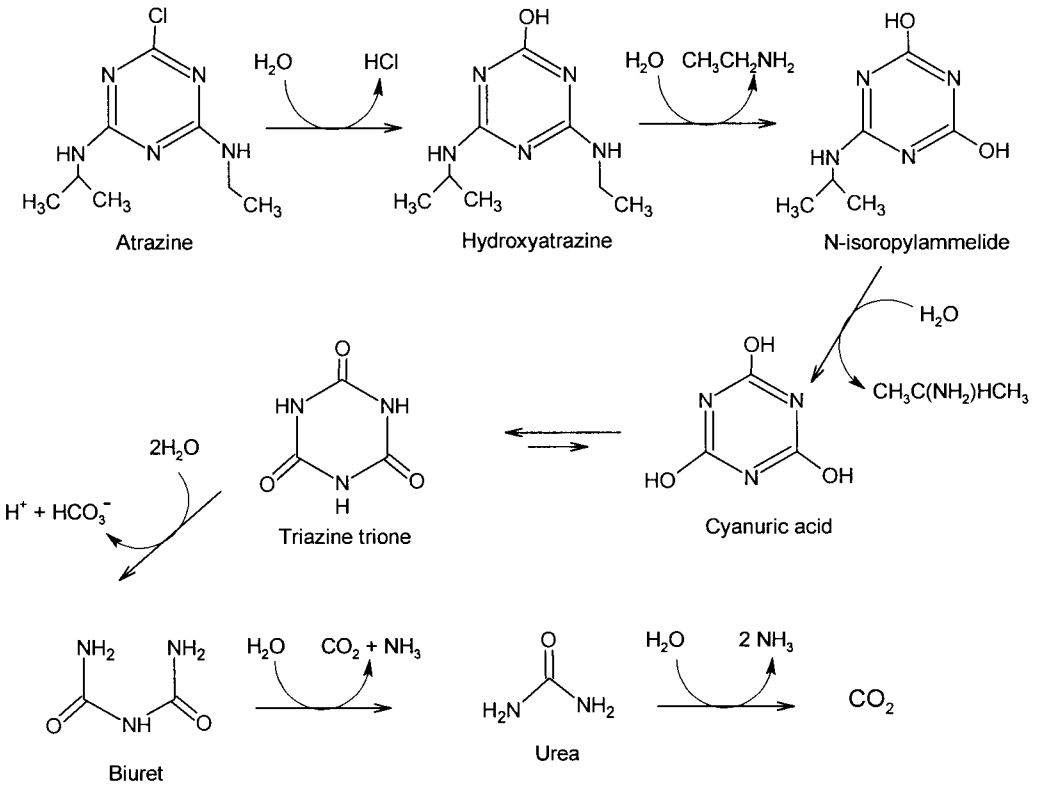


FIGURE 4. Degradation mechanism of atrazine by enzymes. (derived from the University of Minnesota Biocatalysis/ Biodegradation Database).

However, in soil, biological degradation of atrazine is primarily (Levanon,1993) via N-dealkylation (Boundy-Mills *et al.*,1997). Many microorganisms do not further metabolize the dealkylated degradants (Shao *et al.*, 1995).

1.2. Abiotic Remediation

Many abiotic remediation processes have been explored to remove atrazine from waters and soils, including ozone oxidation, acid/base catalyzed degradation, degradation by Fenton's reagent, UV degradation with hydrogen peroxide, sonolysis, atrazine, TiO_2/UV photocatalysis, polyoxometalate photocatalysis, as well as zero valent metal reduction.

Followings are some names, abbreviations of atrazine and the degradants produced in this section:

TABLE 2. Some names, abbreviations of atrazine and degradants

Atrazine	2-cholo-4-(ethylamino)-6-(isopropylamino)-s-triazine	CIET
Atrazine amide	2-acetamindo-4-chloro-6-(isopropylamino)-s-trazine	CDIT
Deethylatrazine	2-amino-4-chloro-6-(isoproylamino)-s-triazine	CIAT
Simazine amide	2-acetamido-4-chloro-6-(ethylamino)-s-triazine	CDET
Deisopropylatrazine	2-amino-4-chloro-6-(ethylamino)-s-triazine	CEAT
Hydroxyatrazine amide	2-acetamido-4-hydroxy-6-(isopropylamino)-s-triazine	ODIT
Deisopropylatrazine amide	2-acetamino-4-amino-6-chloro-s-triazine	CDAT
Chlorodiamino-s-triazine	2-chloro-4,6-diamino-s-triazine	CAAT
Ammeline	2,4-diamino-6-hydroxy-s-triazine	OAAT

1.2.1. Acid/Base Catalyzed Hydrolysis

Hydrolysis of atrazine (Plust *et al.*, 1981) is one of pathways for chemical degradation. Both acid and base can catalyze the reaction (Paris *et al.*, 1973). In weak acid solution, a proton bonding to triazine ring makes it susceptible to nucleophilic subsitution.

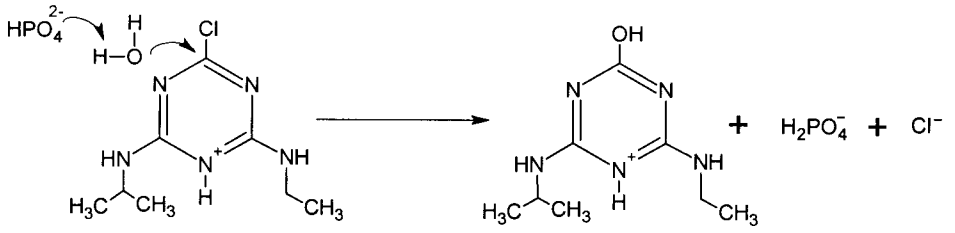


FIGURE 5. Atrazine degradation mechanism in weakly acidic solution

In weakly basic solution, hydroxyl anion can directly replace the chlorine anion. These processes are similar to the degradation in the natural environment.

1.2.2. Promoted Photodecomposition of Atrazine (AZ)

Photolysis includes direct photodecomposition and indirect photodecomposition. Direct absorption of sunlight energy to induce chemical reaction plays no significant role in atrazine degradation. Naturally, in sunlight, wavelengths below 290 nm are not significantly available due to absorption by the ozone layer (Miyamoto, 1996). Helz *et al.*, (1994) studied the direct photolysis at 254 nm. Larson *et al.* (1991) explored a ferric ion promoted indirect process (Figure 6); direct sunlight and a mercury arc lamp were used

for both indoor and outdoor tests. Their results show a similar mechanism (Figure 6).

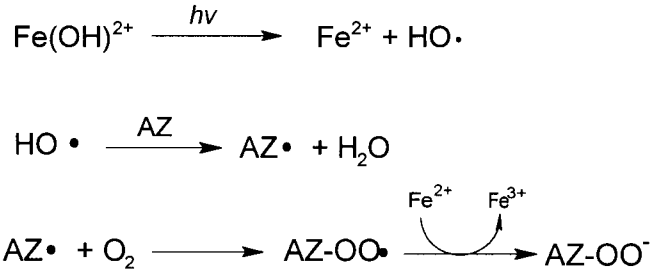


FIGURE 6. Mechanism of ferric ion promoted photodecompostion of atrazine (Larson *et al.*,1991).

Their results shows that lack of oxygen will decrease both atrazine/ferric sulfate and atrazine peroxide reaction since oxygen can react with Fe^{2+} in the dark to generate superoxide ($^{\bullet}O_2^-$) and its conjugate acid $HOO^{\bullet}$ is ready to disproportionate to hydrogen peroxide and oxygen (Bielski, 1978). Reported final products (Figure 7) still contain chlorinated triazine rings.

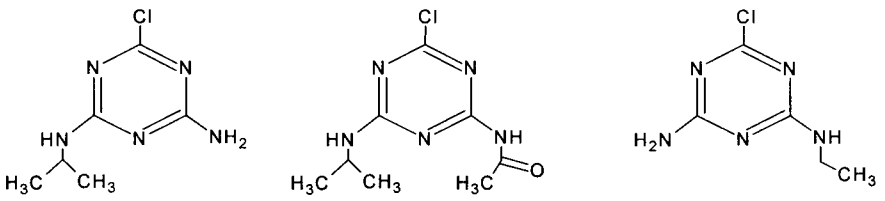


FIGURE 7. Reported final products of ferric ion promoted photodecomposition of atrazine

Balmer *et al.*(1999) found that in the presence of oxalate, this reduction was far more efficient due to the formation of Fe(III)-oxalate complexes, which were more efficiently photolyzed.

1.2.3. Ozonation of Atrazine

The general reactions are as following (Berltrán *et al.*, 1994):

$$AZ + nO_3 \longrightarrow \text{Intermediates}$$

$$AZ + OH\cdot \longrightarrow \text{Intermediates}$$

$$OH\cdot + \text{Intermediates} \longrightarrow \text{final or more intermediates}$$

$$O_3 + OH^- \longrightarrow HO_2^{\cdot} + O_2^{\cdot -}$$

FIGURE 8. Ozonation mechanism of atrazine degradation. n: stoichiometric ratio, AZ: atrazine.

Hydroxyl radical OH· comes from the decomposition of ozone. The initial step is the reaction of O_3 with OH^-.

High pH would promote the reaction possibly due to the contribution of OH^- to this radical reaction. It is considered that reactions between hydroxyl radicals and intermediates are the termination steps.

The authors studied an O_3/UV (254 nm) system and the result showed that ultraviolet irradiation accelerated the photodecomposition significantly due to the appearance of

hydrogen peroxide ion, HO_2^-, which may react with ozone to facilitate later propagation steps.

The order of degradation efficacy was:

UV/Ozonation > Ozonation> Direct Photolysis

The detailed pathways and degradants via O_3 process are shown in Figure 9.

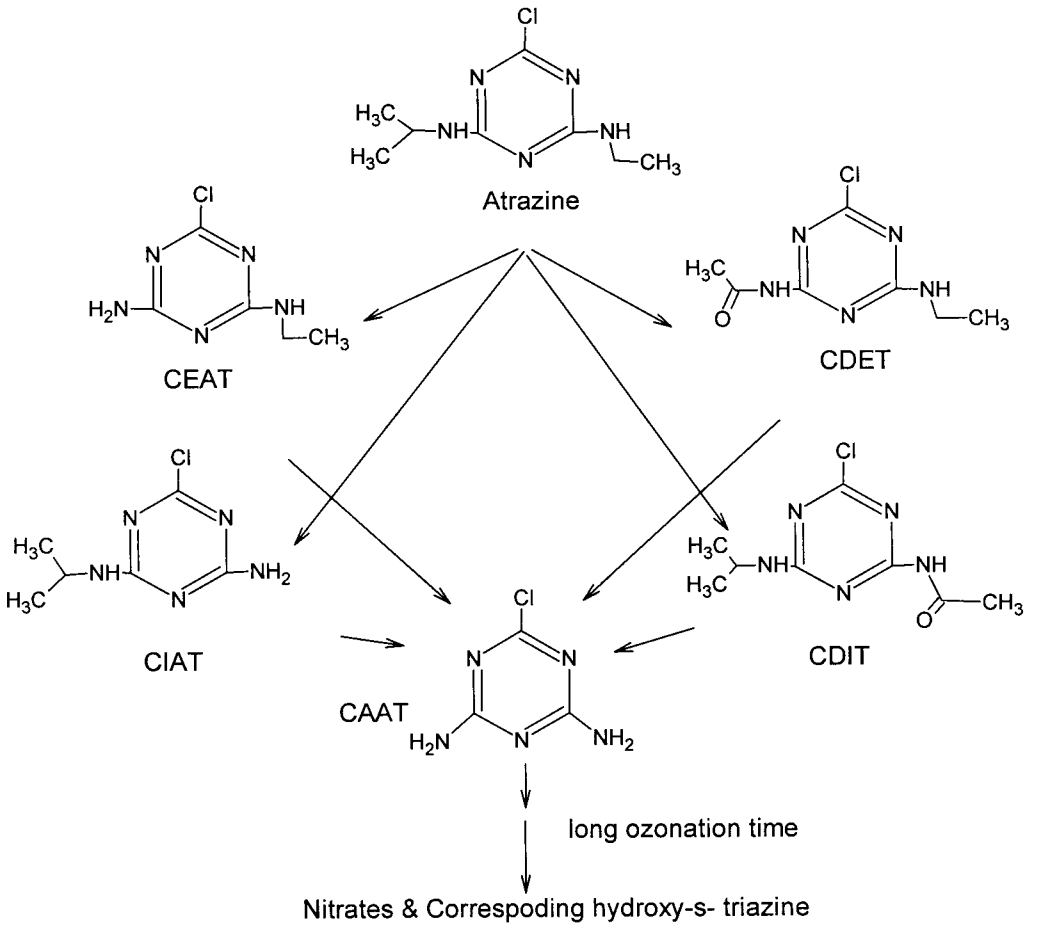


FIGURE 9. Ozonation product pathways of atrazine (Hapeman-Somich *et al.*,1992)

1.2.4. H_2O_2 / UV Oxidation

The possible pathway (Beltrán *et al.*, 1993; Arántegui *et al.*,1995) is as following:

$$\text{Atrazine} \xrightarrow{h\nu} \text{Atrazine}^*$$

$$H_2O_2 \xrightarrow{h\nu} H_2O^*_2$$

$$\text{Atrazine}^* \longrightarrow \text{Products}$$

$$H_2O^*_2 + \text{Atrazine} \longrightarrow \text{Products}$$

The degradants are very similar to those (Pelizzetti *et al.*,1990) found in TiO_2 /UV oxidation process. Two scavengers, bicarbonate ion and humic substances were investigated and the result showed that they could stablize the atrazine by competing with it for hydroxyl radicals.

Beltrán *et al.*(1993) indicated that hydrogen peroxide does not oxidize atrazine but when combined with UV radiation, the rate of the atrazine oxidation increased extraordinarily compared to the simple direct photolysis. Further study showed that the main pathway of this oxidation was carried out through hydoxyl radical attack since hydoxyl radical scavengers, like bicarbonate and humic substancees, would significantly slow down the reaction.

1.2.5. Degradation by Fenton's Reagent ($FeSO_4$:H_2O_2, Arnold *et al.*,1995)

Many metals have special oxygen transfer abilities that facilitate hydrogen peroxide use. However, iron is most commonly used to generate the highly reactive hydroxyl

radical ($OH^{\cdot}$). Although this reaction was found by Fenton, H.J.H. in 1894, its actual use was realized 30 years later, when the mechanisms were understood. It is widely used today to treat industrial wastes.

General overview:

$$Fe^{2+} + H_2O_2 = Fe^{3+} + HO^{\cdot} + HO^{-}$$

$$Fe^{2+} + HO^{\cdot} = Fe^{3+} + HO^{-}$$

The following pathway (Figure 10) shows the detailed process of the side chain oxidation by Fenton's Reagent.

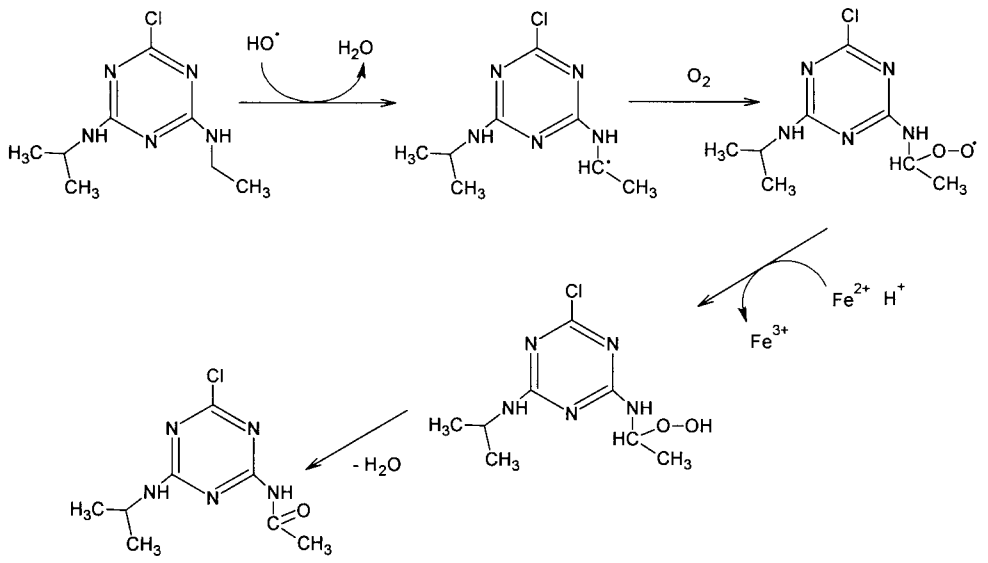


FIGURE 10. This pathways shows that Fenton's Reagent could also initiate atrazine alkylamino side chain oxidation.

The overall proposed degradation pathways by Fenton's Reagent (FR) are the

following (Figure 11). Both dechlorinated and dealkylated products were identified by HPLC/ES/MS/MS or GC/MS. Dechlorination of the alkylated s-triazine derivatives is very likely [II]. Degradation reaction set [I] leading to side chain dealkylation probably occur similarly to dechlorinated derivatives (showed as the dash lines).

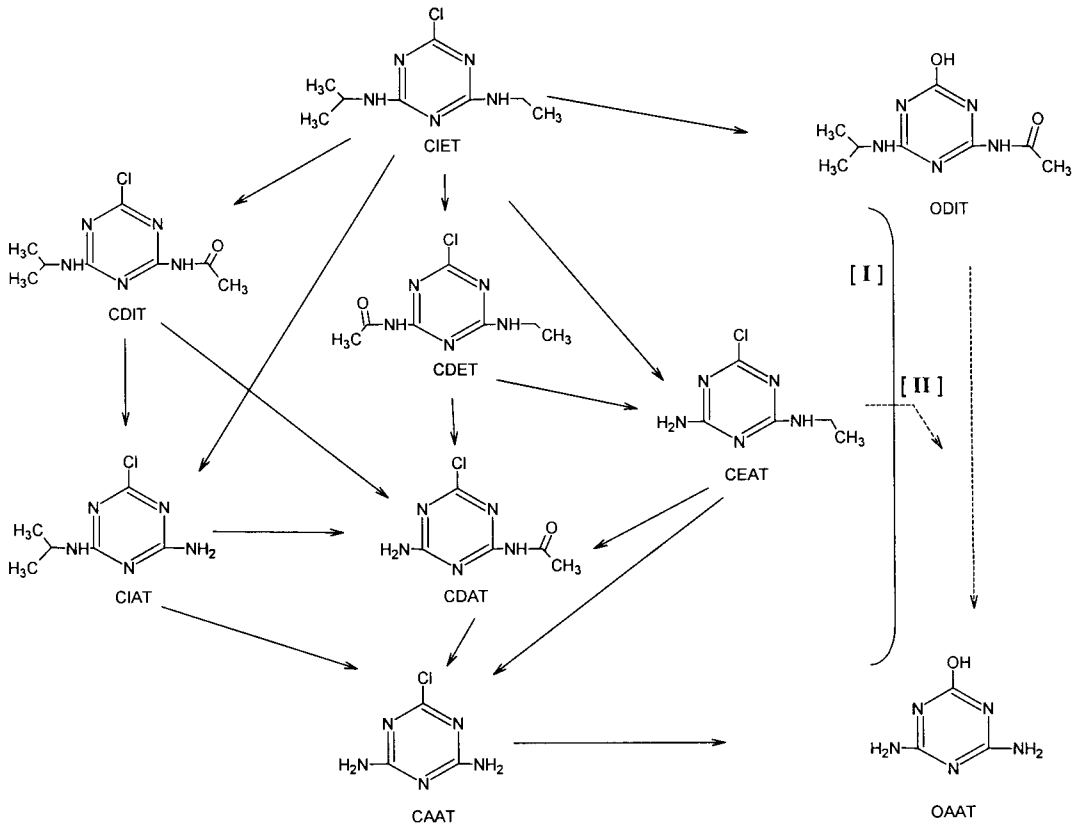


FIGURE 11. Atrazine degradation pathway by Fenton Reagent. 7 products in set [I] including ODIT were well detected. Dashed lines show possible degradation pathways.

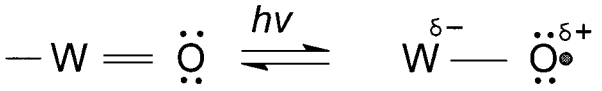
The pathway (Figure 11) set is built by degradants detected and dash lines show possible pathways. Arnold *et al.*,(1995) indicated that the $FeSO_4$:H_2O_2 ratio and pH all affect the

atrazine degradation. Lowering the ratio improves the reaction efficiency due to the less Fe^{2+} to compete for $HO^{\bullet}$ with atrazine, while excess may favor dealkylation. Their study also shows that FR efficiency declined as pH increased.

The main mechanism of Fenton's Reagent is through the hydroxyl radical ($HO^{\bullet}$). The reaction goes rapidly once it begins. The major terminal products are CDAT and CAAT. Further degradation of these chlorinated s-triazines is difficult; dechlorination of alkylated s-triazines is not complete. The over all degradation result is lower than other advanced oxidation process, like TiO_2/UV, possibly due to the lack of photolysis.

1.2.6. Polyoxometalate ($SiW_{12}O_{40}^{4-}$)—Supported UV Photolysis

Polyoxometalates (POM) are metal-oxygen cluster anions formed by acid condensation of pure MoO_4^{2-} and WO_4^{2-}. A typical example is $W_{10}O_{32}^{4-}$. Original solution containing a heteroatom, like silicon, can produce a heteropoly compound ($SiW_{12}O_{40}^{4-}$). The most important property of POM is in the field of photocatalyst (Pope *et al.*, 1991). Illumination upon POM can cause mainly 3 transitions: ①M—M charge transfer (CT), ②d—d transition and ③O→ M CT band. The photoactive charge transfer is the O→ M band at UV and near-visible region, resulting in separation of electrons and holes (Minero *et al.*, 1997, Hiskia *et al.*, 2001):



These complexes then become very powerful oxidants, ready to mineralize a great many organic pollutants (Helz *et al.*, 1994; Mylonas *et al.*, 1996).

The initial step is the UV absorption in metal-oxygen bond of POM(polyoxometalates). NMR data (Fox *et al.*,1987) suggest the formation of preassociated complex of POM and organic substrate in aqueous solution. The oxidation of the associated organic species is mainly through hydroxyl radicals, which are formed by the reaction of the excited photocatalyst (POM) with H_2O (Figure 12).

$$POM \xrightarrow{h\nu} POM^*$$

Direct reaction (S= organic pulltant):

$$POM^* + S \longrightarrow POM(e^-) + S_{ox}$$

Indirect reaction:

$$POM^* + H_2O \longrightarrow POM(e^-) + OH^\bullet + H^+$$

Reaction of hydroxyl radical with S:

$$OH^\bullet + S \longrightarrow \text{oxidation products}$$

Regeneration of catalyst:

$$2\,POM(e^-) + 1/2O_2 + 2H^+ \longrightarrow 2POM + H_2O$$

FIGURE 12. The photodegradation mechanism of POM. The process is mainly through hydroxyl radical.

Generally, this photoxidation reaction includes: (a) hydroxylation of aromatic compounds; (b) decarboxylations; (c) dehalogenation; (d) aromatic ring breaking; (e)

H-abstraction.

Hiskia *et al.* (2001) further indicated that the superoxy radiacal is formed in the process,

$$POM\,(e^-) + O_2 \longrightarrow POM + O_2^-$$

which may further participate in the oxidation processes.

The products involved in POM process of atrazine are as following (Figure 13):

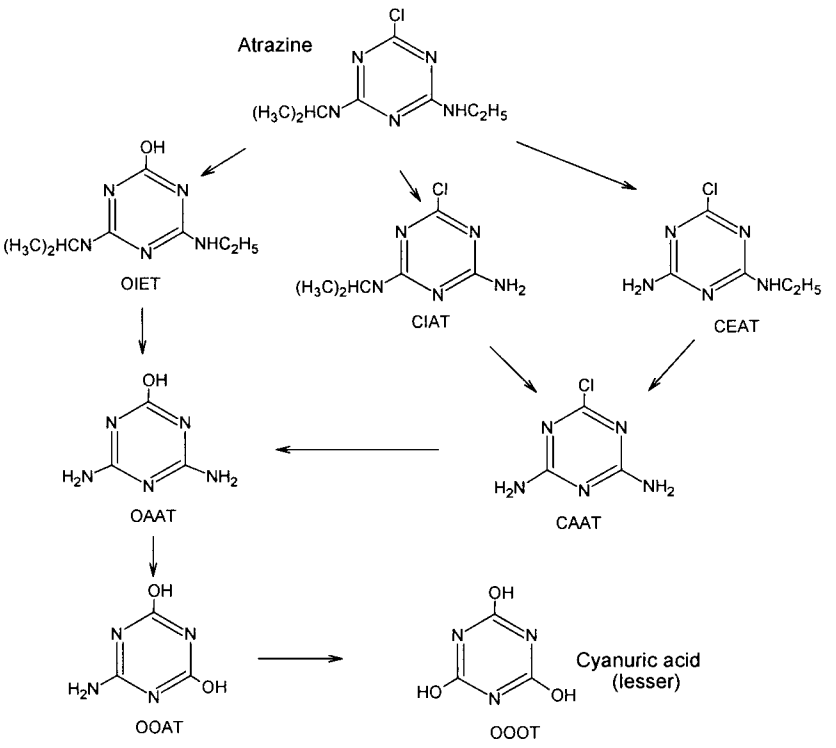


FIGURE 13. The proposed degradation pathway via POM process

1.2.7. TiO_2 /UV Photocatalytic Degradation

Titanium dioxide has been widely investigated for the purpose of photocatalytic decomposition of organic pollutants in water, including atrazine (Minero *et al.*, 1996, 1994, 1992, 1995 and Pelizzetti *et al.*, 1992, 1991):

When photons from the UV radiation excite the electrons at the titanium surface to overcome the "Band Gap" of 3.2 eV (λ = 385nm)(Martin *et al.*,1996), and transfer electrons from "the Valence Band" to "the Conduction Band", holes and free electrons are formed (Figure 14). At this excitation state, TiO_2 works as a powerful oxidizer, actually, a semiconductor catalyst.

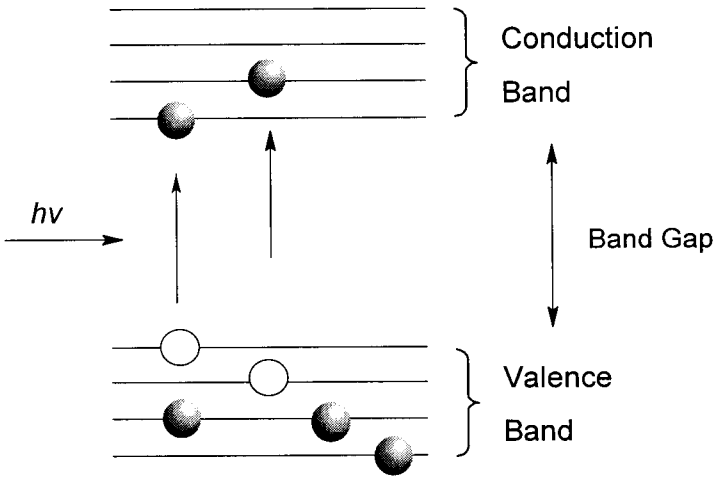


FIGURE 14. Band Transfer of TiO_2 with UV irradiation.

Generally, there are 2 reactions (Kesselman *et al.*, 1997): (1) Positive holes directly oxidize organic pollutants. (2) ·OH-like radicals formed at the conductive band or holes oxidize pollutants (Figure 15).

$$h^+ + R_{aq/ads} \longrightarrow$$

$$OH^{\bullet}_{aq/ads} + R_{aq/ads} \longrightarrow$$

FIGURE 15. Mechanisms incorporating both surface adsorbed and solution phase reaction of TiO_2. h^+: holes; R: organic pollutant; aq: in solution; ads: adsorbed on the TiO_2 surface.

It is reported that the hydroxyl radical reaction is predominant, and the degradants of atrazine are very similar to those in the polyoxometalate process, with cyanuric acid (OOOT) as the major final product (Pelizzetti *et al.*, 1996 and Minero *et al.*, 1997).

Pelizzetti *et al.*(1991) and Sawyer (1991) reported formation of active oxygen species at the conduction band:

$$O_2 + e^- \longrightarrow O_2^- \rightarrow\rightarrow O_2^-,\ HOO,\ HOOH,\ HOO^-,\ HO$$

Gawlik *et al.* (1999) also observed the further degradation of cyanuric acid (OOOT):

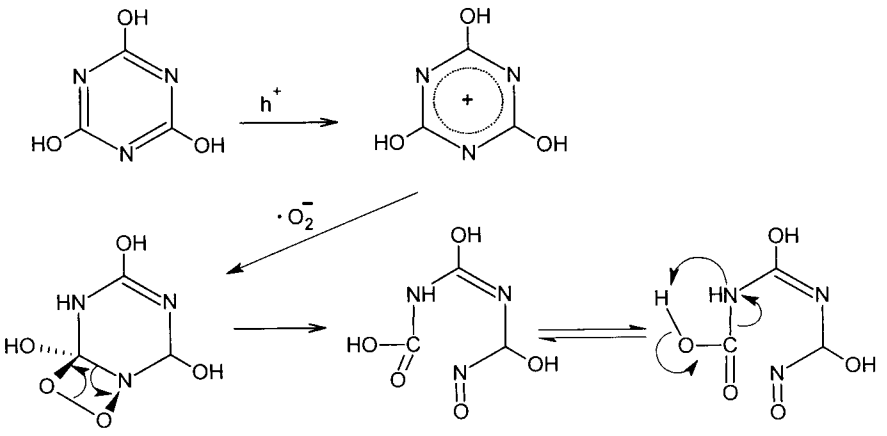


FIGURE 16. Reaction scheme for the photodegradation of cyanuric acid (Gawlik *et al.*,1999)

1.2.8. Sonolytic Decompostion

Sonolytic processes are a subject of sonochemisty, which, defined by Bremner (1990), is a study of chemical effects of sound waves. It is found that ultrasound, 15 KHZ ~ 10MKZ can exert a drastic effect on chemical processes in liquid medium. This is due to the "Acoustic Cavitation Phenomena", characterized by 3 processes: the formation, growth and implosive collapse of gaseous and vaporous bubbles (cavities).

When negative pressure associated with the expansion cycle of the ultrasound wave overcomes the tensile strength of a liquid, the cavities form. During the alternative compression and expansion cycles of the wave, the bubbles continue to absorb the energy of ultrasound until the growing cavities reach a critical size. At this moment, the surrounding liquid rushes into the cavities to cause the implosion. It is so violent (less

than a microsecond) that the implosion causes extremely high temperature (5500℃), pressures (>20 Mpa) and cooling rates (10^{10} Ks^{-1}) (Suslik *et al.*,1989,1990,1991).

This extreme microenvironment can initiate three destructive steps (USACERL 1998):

① Oxidation by hydoxyl radicals:

$$H_2O))))) \longrightarrow H^{\bullet} + OH^{\bullet}$$
$$H^{\bullet} + H^{\bullet} \longrightarrow H_2$$
$$OH^{\bullet} + OH^{\bullet} \longrightarrow H_2O_2$$

Riesz *et al.* (1992) and Makino *et al.* (1983) confirmed that the cavity implosion splits water into hydrogen atoms H·and hydroxyl radicals OH·. The product of hydrogen peroxide is also confirmed. Organic pollutants are highly degradable in this environment.

② Pyrolytic Breakdown:

Pyrolysis is a thermal destruction of compounds in the environment lacking in O_2. The extreme high temperature in bubbles is sufficient enough to decompose many organic compounds (Petrier *et al.*, 1998).

③ Supercritical Water Oxidation (SCWO):

Harradine *et al.* (1993) and Hoffmann *et al.*(1996) reported that during the sonolysis, supercritical water condition (667K, 221atm) is achieved on the estimated 0.0015% of water. Organic contaminants are more soluble in supercritical water and thus are

susceptible to oxidation by oxygen from the dissolved air.

Reported sonolysis of atrazine degradant are:

HA (OIET)

DIA (CAET)

DEA (CIAT)

CAAT

OOAT

Cynauric acid (OOOT) is the final product.

Normally, it is reported that major products of sonolysis are from hydroxyl radical and pyrolysis processes (Petrier *et al.*,1998). Kotronarou *et al.*(1991) indicated that pyrolytic process dominates the high solute concentration, while hydroxyl radical is for low solute concentration.

The above abiotic processes (except acid/basic catalyzed degradation) involved the hydroxyl radical and basically they result in very similar products. They are called advanced oxidation processes. Combined oxidation processes may give a better result (Acero *et al.*, 2000; Nèlieu *et al.*, 2000). Normally, the products of hydroxyl atrazine moieties are the important intermediates.

The main problem for these techniques is the existence of scavengers in natural environment, like humic acids, fulvic acids and bicarbonates, which may terminate the reaction by competing for hydroxyl radicals. So their uses *in situ* may be limited. Also,

under ultraviolet radiation, nitrite formed from nitrate (Beltrán *et al.*,1993; Von Sonntag *et al.*, 1992) should be further considered. Solarska *et al.*(2003) reported that nitrite is formed fast by irradiation of natural water at 254 +185nm, in the process of atrazine treatment. This side-product may cause the fatal condition in infants known as methaemoglobinaemia (Report III, 1996).

1.2.9. Other Removal Methods

Alternative methods for the atrazine removal from groundwater also have been explored, including dialysis (Devit *et al.*, 1998), activated charcoal (Li *et al.*, 2002; 2003), and nano- or ultrafiltration (Majewska-Nowak *et al.*, 2002).

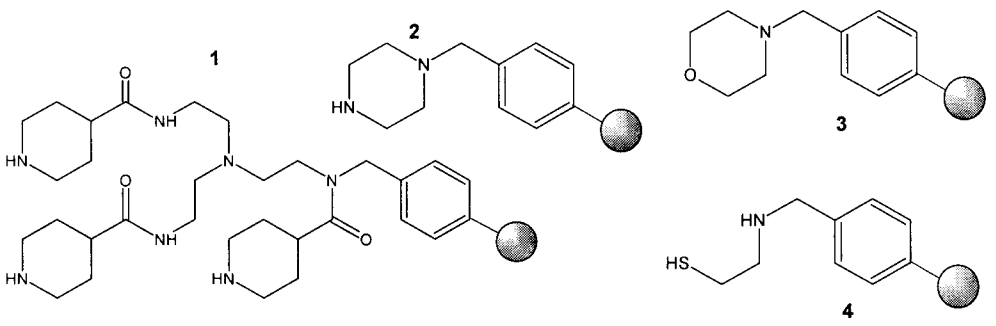
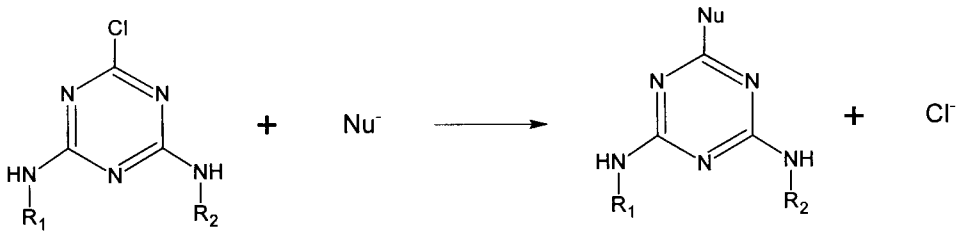


FIGURE 17. Four resins (with solid support), with resin 1 are far more efficient than 2-4 at sequestering atrazine.

Recently, Acosta *et al.* (2004) at Texas A&M University developed a novel removal strategy based on the electrophilicity of monochlorotriazines. Polystyrene resins were

employed as select nucleophiles (Figure 17).

The mechanism in the test is the substitution of chlorine under ambient condition by amine nucleophiles (resins) to form a covalent bond and thus to remove the atrazine and its degradants from contaminated water (Figure 18).



Atrazine	R_1= ethyl;	R_2 = isopropyl
Deethylatrazine	R_1= H;	R_2 = isopropyl
Deisopropylaztrazine	R_1= ethyl;	R_2 = isopropyl

FIGURE 18. Nucleophilic substitution of atrazine and its degradants. Nu^-: nucleophiles (resins).

Water pH and ionic strength have little influence on the sequestration of atrazine. Solid supports with higher surface significantly facilitate this process and choices can be clays, silica gels and mesoporous silicas, etc. However, the incineration of the waste remains a problem.

1.3. Zero Valent Iron Reduction

Since Sweeny and Fisher first reported environmental application of Fe metals in the

patent literature (1972), works using zero valent metal for environmental remediation of organic contaminants has attracted considerable attention. In the remediation with a study of ground water, Gillham and co-workers (Reynolds *et al.*, 1990, Gillham *et al.*, 1994, Gillham, 1995) observed that halogenated hydrocarbon solvents were unstable in the presence of zero-valent metals. Further study showed that the apparent degradation was due to dehalogenation in which galvanized steel, stainless steel, aluminum, and iron could be involved.

Since zero valent Fe^0 metal reduction is (1) inexpensive, (2) nontoxic, (3)faster and more energy effective than biotic remediation, (4) simple and requests no expensive facilities, and (5) environmental friendly, it has excellent potential for the treatment of atrazine contaminated ground waters and surface waters. Naturally existent humic and fulvic acids in water and soil may present necessary acidity (H^+)(Schnitzer *et al.*, 1978).

1.3.1. Chemical Background of Fe^0 Process

The redox couple is formed by Fe^0 and dissolved Fe^{2+}:

$$Fe^{2+} + 2e^- \longrightarrow Fe^\circ$$

Standard reduction potential: -0.440 V

With such a negative potential, Fe^0 is ready to reduce many redox-labile substances.

Alkyl halides, RX, can be reduced by Fe^0 dehalogenation:

$$RX + 2e^- + H^+ \rightarrow RH + X^-$$

Estimated standard reduction potential: +0.5 ~ +1.5 V at pH 7 (Vogel *et al.*, 1987).

There may be a second reaction:

$$RX + 2Fe^{2+} + H^+ \rightarrow RH + 2Fe^{3+} + X^-$$

Dissolved Fe^{2+} is also a reductant to some alkyl halide. However, the process may be very slow (Doong *et al.*, 1992 and Klečka *et al.*, 1984).

Whether or not "nascent" hydrogen (hydrogen produced immediately in the reaction), is involved in the reductive dehalogenation remains of interest. However, such a process normally needs a catalyst (House, 1972). Generally, the direct electron transfer model is preferred:

$$RX + 2Fe^0 + H^+ \rightarrow RH + 2Fe^{2+} + X^-$$

Many articles indicate that a wide variety of organic compounds, including halogenated aliphatics, polyhalogenated aromatics, such as PCBs, DDT and atrazine could be reduced in a similar way (Zawaideh *et al.*,1997). The detailed mechanism of

these reactions, however, is not very clear.

Dombek *et al.* (2001) studied the dechlorination process of atrazine with zero valent Fe^0 and found that this degradation process was mainly controlled by the pH of the solution. It was believed that atrazine was protonated first and then went through the reduction process:

$$[H - Atr - Cl]^+ + Fe\ (s) \longrightarrow Atr - H + Fe^{2+} + Cl^-$$

1.3.2. Mechanistic Insight

The approach of Fe^0-amended remediation has been developed originally from removal processes of a wide arrange of halogenated aliphatic compounds from contaminated water, such as 1,1,2,2-tetrachloroethane, trichloroethane (TCE) (Senzaki *et al.*, 1988; 1989), and chlorinated methanes (Matheson *et al.*, 1994).

Roberts *et al.* (1996) and Arnold *et al.* (2000) did intensive work in order to understand the mechanism. Their early study on *trans*- and *cis*-DCE (dichloroethylene) suggested the following pathways (Figure 19):

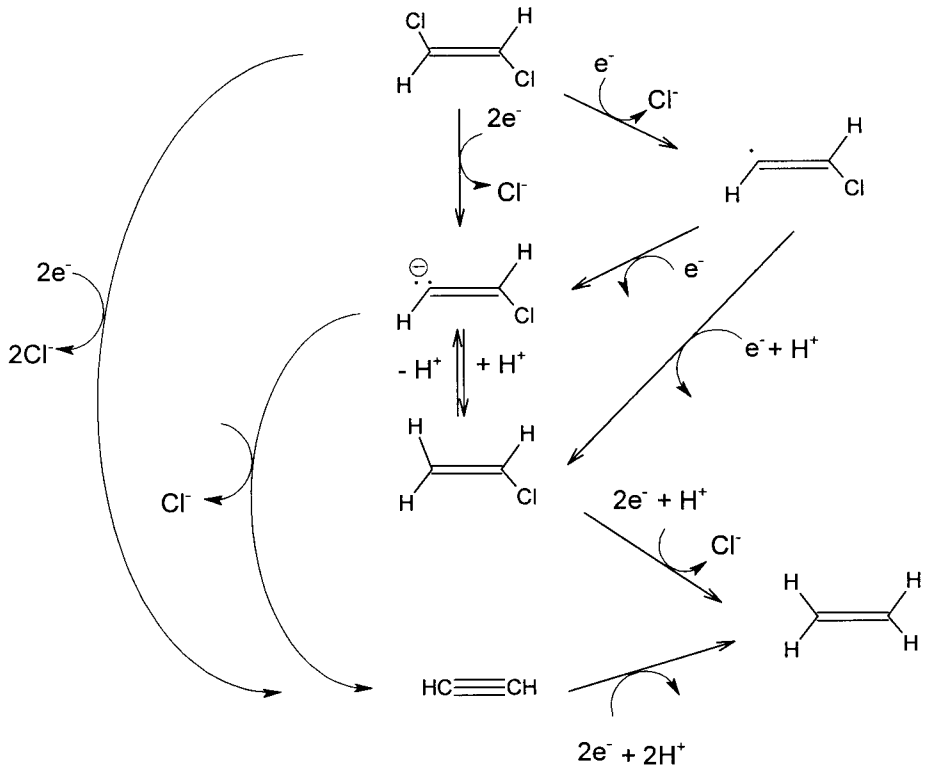


FIGURE 19. Proposed pathways for Fe-metal reduction of *trans*-DEC

The reaction was carried out via transfer of 2 electrons from Fe^0 to form a free radical, and followed by either β-elimination or a hydrogenolysis process.

Their later work was focused on the Fe^0 metal surface. The high reactivity of *cis*-vinyl halides (*cis*-1,2-dichloroethene) strongly suggested a surface-mediated reaction. At least three steps were involved: (a) adsorprtion (b) reaction (c) desorption. This mechanism implied that a direct electron transfer at the reactive site on Fe^0 surface was necessary. The rate-limiting step is the formation of the di-σ-bond (see Figure 20 for similar scheme using tetrachloroethylene).

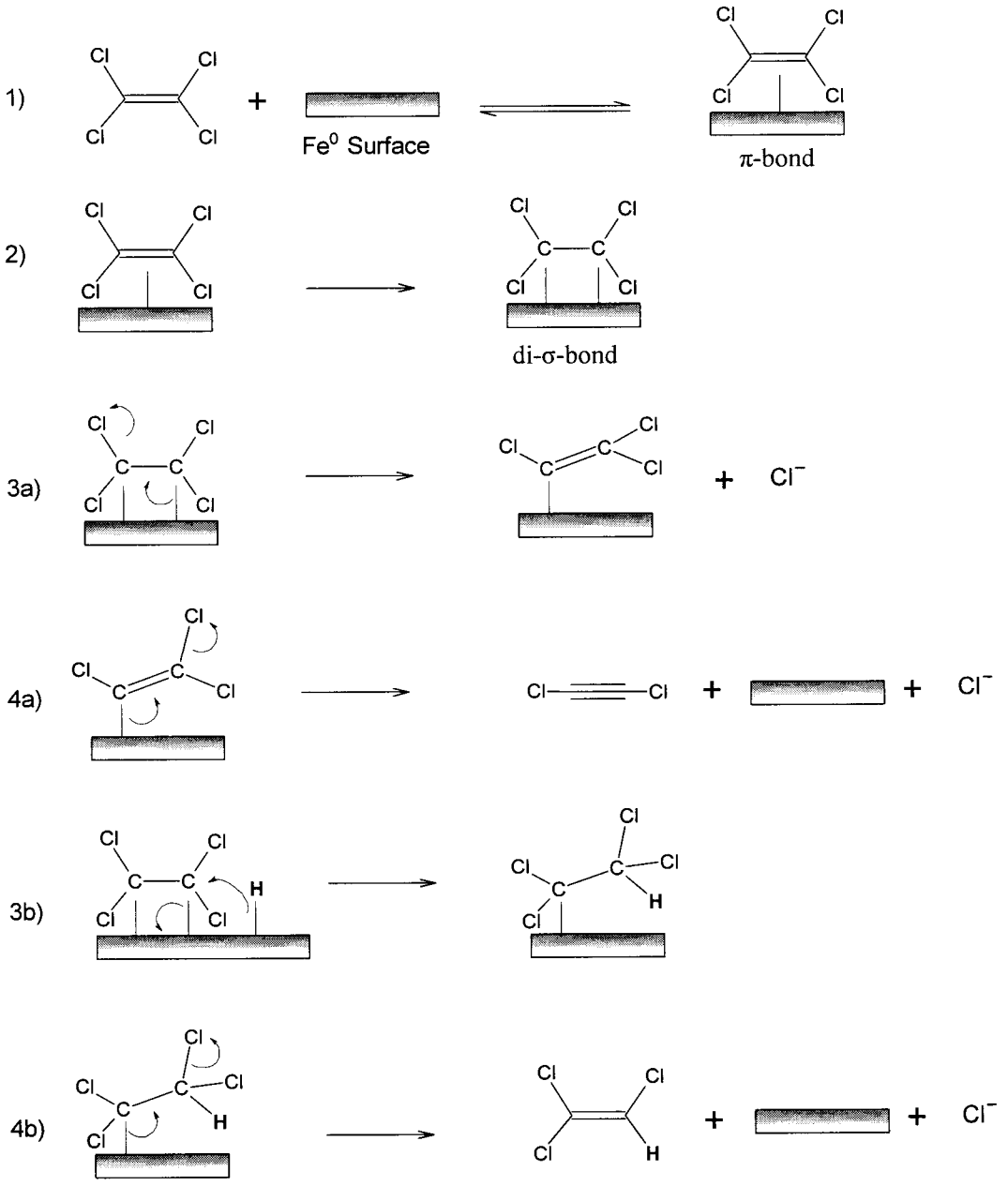


FIGURE 20. Hypothesized pathways for reduction of tetrachloroethylene on Fe^0 surface

However, another independent study conducted by Weber (1996) proposed an alternative mechanism other than surface-mediated process. To investigate the possibility

of circumventing the direct contact of organic pollutants with the Fe^0 surface, a probe molecule, 4-aminoazobenzene (4-AAB), was chosen. The results showed that natural organic matter (NOM) could function as electron mediators to shuttle electrons from a bulk Fe^0 surface (electron donor). And thus the electron-mediated reduction arises (Figure 21).

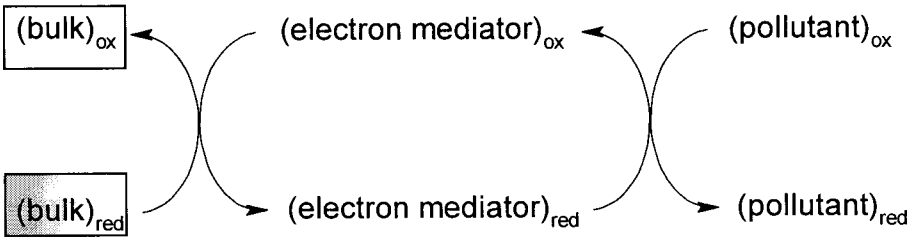


FIGURE 21. Electron-mediated process for Fe^0 metal remediation

This approach is of great significance to extend the zero valent iron technology since it may not be necessary for all kinds of organic contaminates to adsorb on or directly contact reactive sites of Fe^0 surface. Thus agrochemicals, which are strongly absorbed to NOM in sediment and soil, may still undergo reduction without direct contact of Fe^0 due to the existence of humic and fulvic acids as mediators.

1.3.3. Permeable Barrier

The promising use of zero valent iron for remediating contaminated water has

caused a lot of attention, and numerous field and lab studies have been conducted to evaluate the feasibility of this approach. Building a permeable wall of Fe^0 to intercept plume of contaminated ground water was proposed (Roush, 1995; O'Hannesin *et al.*, 1998). Up to 2003, more than 48 test installations have been completed in the world (Roberts *et al.*, 2003). It is believed that the implementation of Fe^0 permeable barriers (Figure 22) could remediate water contaminated by agrochemicals to "a regulatory concentration level" and with "extremely low cost" of maintenance (EPA/600/R-98/125, 1998).

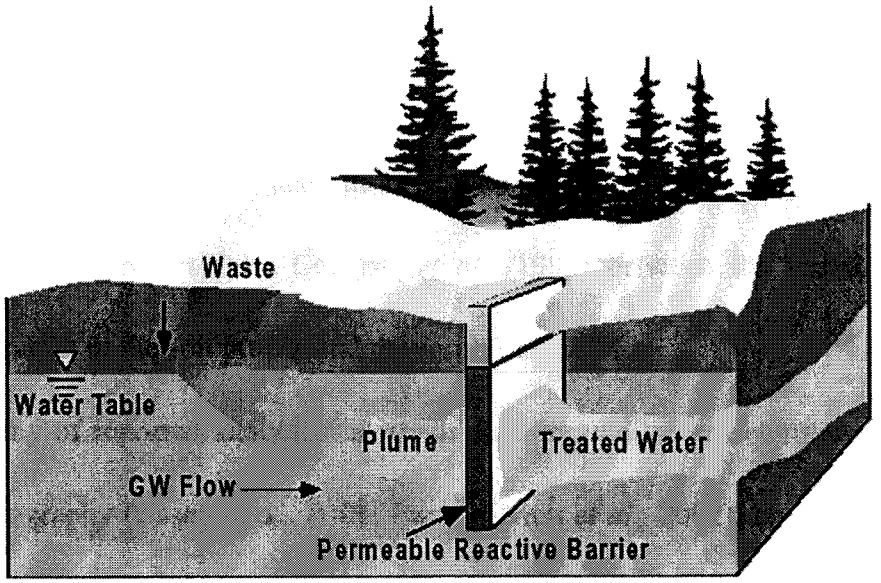


FIGURE 22. A pilot Fe^0 permeable barrier implementation (EPA)

1.4. Br^- Tracer by XRF

Bromide has been widely used to monitor and predict water and nutrient transportation in agricultural and environmental investigation since it is free from chemical and biochemical transformation in natural soils (Bowman, 1984; Owens *et al.*, 1985). Foussereau *et al.* (1997) and Paramasivam *et al.* (1999, 2002) pursued field studies to understand the intrinsic spatial and temporal variability of Br^- tracer through the vadose zone in citrus groves. By comparing the concentration ratio of NO_3^--N with Br^- after their simultaneously application in the fields, an effective model of N-dynamics in soils could be built (Paramasivam *et al.*, 2002; Casey *et al.*, 2001).

To improve agriculture practice, a solute transport model, the Leaching Estimation and Chemistry Model (LECM, by Wagenet *et al.*, 1989), has been widely employed to assess the fate of contaminates in soils (Soulshy *et al.*, 1992; Jabro, 1993). A good agreement was reported by Comfort *et al.* (1993) between the measured Br^- tracer concentration in the soil profile and the result of LECM.

Many of reported analytical methods for bromide tracer determination are via ion chromatography (Casey et al., 2001; Paramasivam *et al.*, 2002), but some are also using ion selective electrodes (McLeod *et al.*, 2001). Measuring bromide tracer by X-ray Fluorescence also is feasible. X-rays are short wavelength electromagnetic radiation (10^{-5}Å~100 Å), and can produce either continuous spectra or line spectra. When bombarding electrons collide with target metal atoms repeatedly, continuous radiations

are produced (Skoog *et al.*, 1992). Discrete line spectrum arises when the bombarding electrons have sufficient energy to take one of the inner orbital electrons out and the outer orbital electron then transits to the vacant orbital, which is associated with the emission of X-ray photons. Since the energy levels (K, L, M...) are solely the characteristic of a target atom, the line spectrum is independent of the physical and chemical state of the atom. So the characteristic line spectrum of X-rays offers a reliable way to trace an atom. X-ray fluorescence (XRF) thus involves a process of absorption of X-rays and then emission of X-ray photons at longer wavelengths. Each element displays a characteristic XRF spectrum.

Bromine tracer, with well-established X-ray fluorescence analysis, has been used as a new approach for tracing of sea-salt routines in ancient culture (Aloupi *et al.*, 1998). The similar approach has recently been applied in studying the cycling of inorganic bromine in the marine boundary layer (Sander *et al.*, 2003). The reported detection limit of Br can be as low as 0.5~0.6 ppm (Report IV, V).

1.5. Statement of Purpose

The purpose of this work was to investigate the details of atrazine degradation and to explore the feasibility of applying a Fe^0 column process for on-site remediation of atrazine. Of particular interest was the degradation efficacy and effects of different initial pH, length of the Fe^0-sandy column, and flow rates. NaBr was used as a tracer to indicate

the column diffusion properties and an XRF analytical method for this purpose was established. X-Ray Fluorescence, HPLC and GC-MS were the main methods used to analyze degradation results. Solid Phase Extraction, LC/MS and TLC were also employed. Batch reactions were carried out to compare with the column results and help delineate a possible degradation pathway. Based on these studies, guidelines can be obtained for the design of a column system aimed at the on-site remediation of atrazine-contaminated water.

2. MATERIALS AND METHODS

2.1. Atrazine Degradation in Solution

2.1.1. Stability Test

The atrazine stock solution was made by placing 4.0x10 mg of atrazine (99%, Pfaltz & Bauer, Inc.) in a 100-mL volumetric flask and diluted to volume with a 50% methanol/50%water solution to give a final concentration of 4.0 $x10^2$ μg/ml (400 ppm). 10 mL of atrazine solution (400 ppm) was pipetted into a different 100 mL volumetric flask, diluted to volume with aqueous solutions of pH 1.4, 1.6, 2.0, 4.0, 6.0, 8.0 (the acidity was pre-adjusted by 1.0 M H_2SO_4 solution or 0.10 M NaOH solution). Each solution had a similar concentration of 4.0x10 ppm atrazine and was stored in a brown glass bottle (capped) and left on the bench top in the lab at room temperature 25 °C. For each solution, 0.50 mL aliquots were removed at day 0, 5, 10, 15, 20 respectively; and samples were analyzed by HPLC at each sampling time.

2.1.2. Acidity Solution Reaction (with Fe^0)

In a 300 mL 3-neck flask, 1.0x10 g Fe powder (Fisher, ≤ 100 mesh) was loaded and 200 mL pH 2.0 de-ionized water (acidity adjusted by H_2SO_4) was added. The solution was kept under stirring for 10 min and the upper layer of solution was carefully poured out. Then 3 portions of 100 mL deionized water (degassed by N_2 purge to drive out

dissolved O_2) were employed to wash the surface of the Fe powder three times and the wash solution was discarded as much as possible.

200mL of atrazine solution(4.0x10 ppm, NaBr $1.2x10^2$ ppm) was added and the reaction solution was stirred at 200 rpm (Yamato LR 500B stirrer). A control reaction was set with 200 mL of 4.0x10 ppm atrazine but no NaBr. Several drops of concentrated H_2SO_4 were added to keep the acidity stable and pH value was monitored by a pH electrode (Accumet) with a pH meter (Accumet pH meter 915).

The reaction was conducted under a blanket of N_2 gas to avoid iron oxidation.

Every 30 min, a 2.0 mL aliquot was pipetted into a 5 mL syringe then filtered with a 0.02μm membrane filter. 0.5 mL filtrate was put into a HPLC vial for HPLC analysis. The remaining filtrate was used for the XRF test (see section 2.2.).

At the end of reaction, the whole reaction solution was filtered through a Buchner funnel (55 mm). The solution then was run through a solid-phase extraction cartridge. 3 mL of methanol or isopropanol was used to wash out compounds absorbed (see section 2.5.). The eluent was analyzed by HPLC and GC-MS.

A high concentration reaction was also conducted to separate and identify the degradation products. This reaction was carried out similar to the way described above. The initial solution was prepared by dissolving 1.0 g atrazine in 200mL isopropanol and then 100 mL deionzed water was added quickly. 2.0x10 g Fe powder was added and the reaction mixture was stirred at 200 rpm. 2 mL of concentrated H_2SO_4 was added every 30

min until the end of the reaction. The reaction mixture was filtered through a funnel and then distilled by rotary evaporation (Brinkman RE 111). Further vacuum distillation was continued through a vacuum trap system (liquid N_2 as the coolant) for 1 hour. The final distillate was re-dissolved in iso-propanol for TLC and GC-MS analysis.

2.1.3. Degradation in Basic Solution

A reflux apparatus was used with a 250 mL flask. 100 mL of 40ppm atrazine solution and 0.50g of sodium carbonate were added. The reaction solution was agitated and refluxed at 80°C. At 0, 3, 6 hours and one week. Aliquots of 0.50 mL of the reaction solution were removed and analyzed by HPLC immediately after each sampling time.

2.2. Bromide Tracer Test

NaBr Stock Solution. $2.0x10^2$ mg of NaBr was dissolved in a 100 mL volumetric flask and diluted to volume with deionized water. The stock solution had a concentration of 2.0 mg/mL.

NaBr Standard Solution. 0.0, 0.10, 0.20, 0.30, 0.40, and 0.50 mL of NaBr stock solution were pipetted respectively into separate 25 mL volumetric flasks and diluted to volume with deionized water to prepare calibration standard solutions of 0, 0.0080, 0.016, 0.024, 0.032, and 0.040 mg/mL, respectively. A higher concentration series also was

prepared with final concentrations 0f 0, 0.016, 0.032, 0.048, 0.064, and 0.080 mg/mL, respectively.

XRF Sample Preparation. Filter paper (qualitative, 55 mm diameter, Whatman) was cut in circular tipped pieces (25 mm diameter). A small hole was bored into the filter paper by a push pin 2 mm from the edge from the tip.

Each standard solution of 5.0 mL was added to a 50 mL beaker. A piece of cut filter paper was dipped in the corresponding solution for 20 seconds and then was carefully hung in a sealed glass box for 30 min to allow the solution spread evenly and dry out slowly. Finally, the box was opened to let the paper dry out further.

The tip on the paper was cut and then the sample paper was placed (as flat as possible) on a XRF cup (Chemplex, 32 mm diameter, 23 mm high, double open ended) by pieces of X-ray film (Chemplex, Prolenne, gauge: 4.0 μm).

Determination of Bromide. Paper samples were measured by an XRF spectrometer (Spectro, Xepos). The central channel was set at 501 (E/keV:11.919) for measurement of Br^-, with a counting for 30 min. The Br peak was identified in the spectrum and was integrated against the corresponding concentration to obtain the calibration curve. In the column calculation, a simplified single point calibration was adopted.

2.3. Degradation in Packed Column

2.3.1. Column Preparation

Sand (Mallinchrodt chemical, Inc) sieved by a 120 mesh sieve, was pre-mixed with Fe powder (Fisher, 100 mesh). Every 5.0 g or 1.0x10g of sand was mixed with 0.86 or 1.7 g Fe powder in a 100 mL beaker by shaking and then was poured into the column to achieve about 15 % of Fe in the mixture.

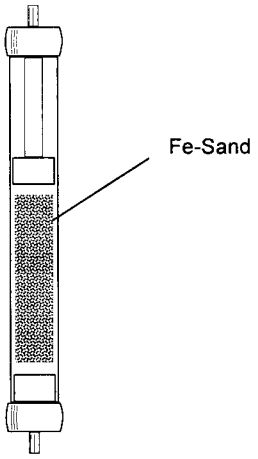


FIGURE 23. Fe-Sand Column

The Fe-Sand mixture was carefully packed into a glass chromatography column (Omnifit, length 250 mm, diameter 25 mm). Two ends of the column was sealed by 10-15 mm glass wool and then with the column filters and caps. Two ways of packing the column were adopted: 1) The whole column: the sand and Fe mixture was filled to 15.5 cm; 2) A half column, 7.5 cm filled with Fe and sand mixture with the rest of the column filled with only sand. The total pack length still reached 15.5 cm.

A blank column was prepared in the same way but only filled with similar amount of sand.

Before the stock solution was pumped through the column, both columns were activated by 200 mL pH 2.0 deionized water (adjusted by H_2SO_4) at the flow rate 9.00 mL/min with an HPLC pump (Beckman, 112 Solvent Delivery Module or Alltech 301

HPLC pump).

2.3.2. Stock Solution

4.0x10 mg of atrazine (Pfaltz & Bauer, Inc.) was weighed on an analytical balance (Sartorius Basic) and was transferred into a long stem glass funnel with clogged glass wool as the filter. The funnel was set on a 1000 mL volumetric flask. 40 mL methanol (AR, 99.8%, Fisher) or acetone (AR, 99.8%, Mallinckrodt) was guided down a glass rod to drop carefully onto the atrazine on the glass wool. The atrazine compound started to dissolve and the residue was completely dissolved and washed down into the volumetric flask. About 800 mL de-ionized water (saturated with N_2 for 30 min to drive out dissolved O_2) was quickly added. Then 6.0x10 mg of NaBr (AR, Fisher) was dissolved and added. De-ionized water was finally added to the volume. The stock solution was placed in the cabinet to avoid light. A typical stock solution contained 4.0x10 ppm atrazine, 6.0x10 ppm NaBr, and 4.0 % Methanol or Acetone.

2.3.3. Sample Collection

After the column was activated by pH 2.0 deionized water (adjusted by concentrated H_2SO_4), the atrazine stock solution was pumped through the column. The flow rates of the pump were set at 0.050 mL/min, 0.10 mL/min and 0.15 mL/min, respectively.

There were 2 ways to control the initial pH of the stock solution pumped in the

column. (1) Pre-mixed Mode: concentrated H_2SO_4 was added directly in

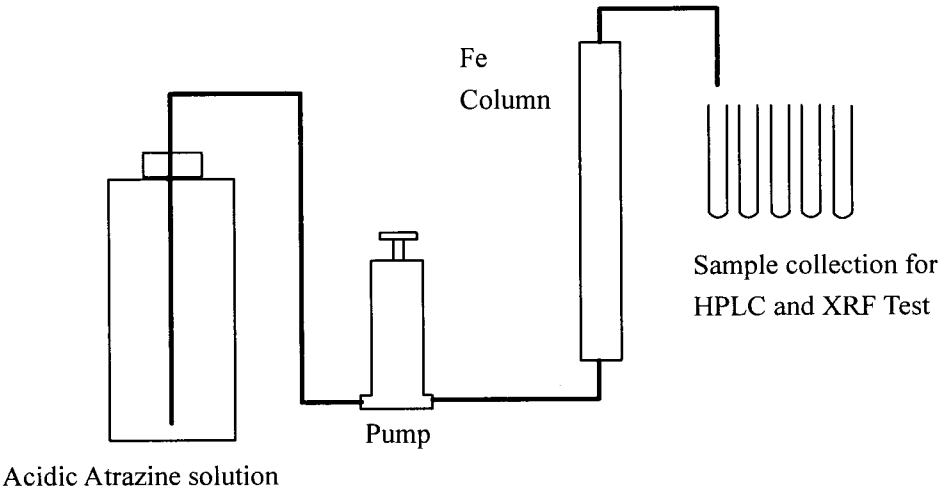


FIGURE 24. Pre-mixed stock solution was pumping in the column.

the stock solution. The acidity was measured by a pH electrode with the pH meter (Accumet pH meter 915, Fisher Scientific). This solution was then pumped through the column (Figure 24).

(2) Jointed mixed Mode: a concentration of atrazine solution (8.0x10 ppm atrazine and $1.0x10^2$ ppm NaBr) was prepared and stored in the bottle #1, acidic water in the bottle #2. When the solution was running into the column, the pump took in both liquids from two bottles and mixed them at the T-valve, where the mixture was then

pumped into the column (Figure 25). The pH of the mixture was measured at the initial time and the end time by switching the mixture to a test tube.

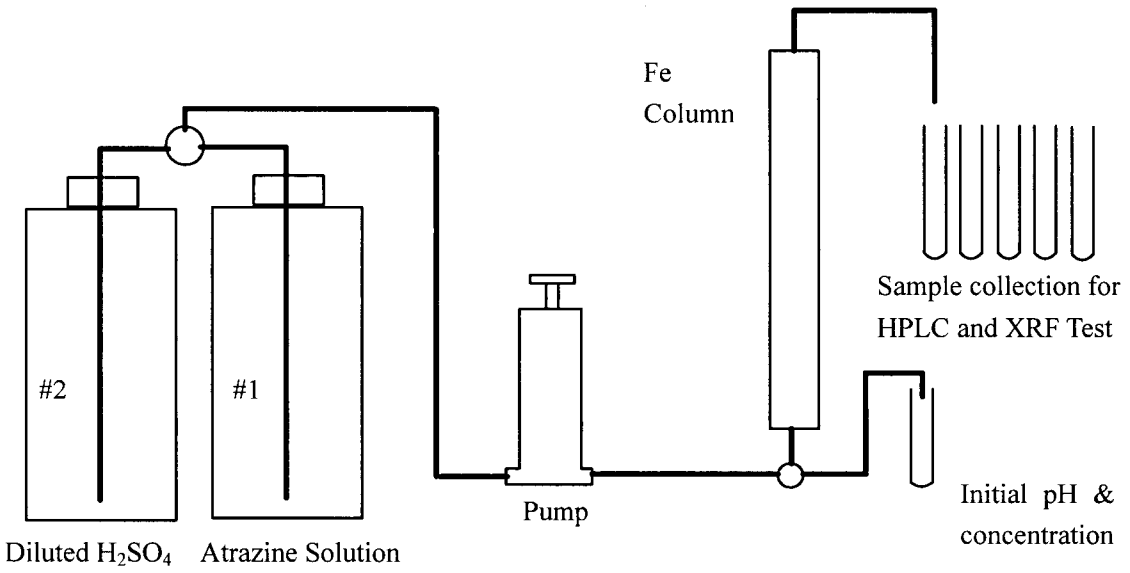


FIGURE 25. Jointer mixed mode: Acidic solution mixes with atrazine stock solution before pumping in to the column.

An array of 10 mL test tubes (volume mark calibrated by a 10 mL cylinder), were ready in a rack to collect the effluent samples, 10 mL each. One drop of 6.0 M H_2SO_4 was added to keep the samples acidic (pH around 2.0). Samples were analyzed by HPLC and XRF.

2.4. Solid-Phase Extraction

The solid phase extraction cartridge (Supelco®, C-8, 3 mL, 6 mL) was set into a funnel and the cartridge was conditioned with 3 ml methanol first and then 3 mL deionized water. The solution was always kept dropping naturally (the cartridge should not be run dry!). The 1~3 mL sample solution was loaded and then run through the cartridge under a proper vacuum in that solution was pulled down by drops. 3 mL deionized water was employed to wash the cartridge under a proper vacuum. Then, the maximum vacuum was used to dry the cartridge sorbent for 5 minutes. The captured compounds (on the sorbent was eluted with 3ml methanol into a glass vial.

The eluted solution was subjected to HPLC, TLC and GC-MS (HP Hewlett 5971 series) analyses.

2.5. Chromatographic and MS Analyses

2.5.1. HPLC

Hitachi 7000 series, with the parameters set at:

C18 column (25cm, Whatman®, Partisphere)

C18 guard column

Flow rate 1.00 mL/min

Injection volume: 20 μL

Column temperature: 30°C

UV detector wavelength: 220 nm

Mobile phase: (1) 80% Methanol, 20% H_2O

(2) 65% Methanol, 35% H_2O

Degas: online

Needle wash solution: Methanol.

2.5.2. GC/MS

HP 5890 Series II GC with a HP 5971 Series Mass Selective Detector.

Column: HP-MS, 30×0.25 mm i.d, 0.25μ film thickness.

Inlet Temperature: 250 °C

Oven Program: 3 min at 50 °C, increase at 20 °C/min for 10 min; held at 250°C for 2 min.

Carrier Gas: Helium

Injection Volume: 20 μL

The mass spectrometer was automatically calibrated before sample test every day.

2.5.3. TLC Analysis

Thin layer chromatography plates (Silica Gel GF, 20x20 cm, 2000 microns and 10x20 cm, 250 microns, Analtech, Inc) and an UV light (254 nm, Mineralight® light) were employed. Trichloromethane (99%, Aldrich) with 5 % methanol was used as the

mobile phase. Sample plates were developed in a sealed chamber. Separated spots or straps were identified under UV light. The spots or straps were scraped out and packed into a 5 mLsyringe with the end filled with grass wool as a filter. 5 mL methanol was used to elute the samples captured into a small vial, which is carefully heated to evaporate the methanol. Sample was re-dissolved into iso-propanol for GC-MS analysis.

2.5.4. LC/MS Analysis

Sample Preparation. 4.0 mg of atrazine was placed into a 100 mL volumetric flask. 80ml of Milli-Q water was added and the solution was sonicated for 15 min. Milli-Q water was used to dilute to the volume. The atrazine solution was isolated from light. A second atrazine solution was prepared the same way but with Milli-Q water adjusted to pH 2.0 by 1.0 M hydrochloric acid.

4.0 mg of 2-Hydroxylatrazine was placed into a 100 mL volumetric flask. 80ml of Milli-Q water was added and the solution was sonicated for 15 min. Milli-Q water was used to dilute to the volume. The hydroxylatrazine solution was isolated from light.

The atrazine and hydroxyl atrazine solutions were sampled at day 0, 1, and 180 and samples were tested by LC/MS.

LC/MS Method. Directly inject the sample solution with a 250 μL syringe at 10 μL/min. The LC/MS parameters was set as:

PE, *SCIEX* API 365 LC/MS/MS Triple Quadrupole.

Ion Source: Turbo Spray

Polarity: Positive

Scan Type: Q1 MS (Q1)

Scan Mode: Profile

ResolutionQ1: UNIT

MR Pause: 5.0070 msec

Step Size: 0.1 amu

3. RESULTS

3.1. Degradation in Solution

Atrazine solutions (without Fe^0) at different pH values were tested at 5-day intervals over a 20-day period. The loss of atrazine was indicated by the observed concentration ratio, C/C_0; C was the observed concentration while C_0, the original atrazine concentration. The overall profile of atrazine loss at different pH values is depicted in Figure 26. When ambient pH was below pH 4.0, the concentration of atrazine decreased quickly, especially at pH 1.4, where drastic loss of atrazine was observed. At day 20, the final concentration ratio of atrazine ranged from 0 to 97 % (Table 3). The solution that degraded the most atrazine was at pH 1.4, in which 100 % atrazine was lost, in stark contrast to the solution with ambient pH 8.0 (only 3 % loss).

TABLE 3. Atrazine Stability in Different pH Solution

	C/C_0 *					
Time (days)	pH 8.0	pH 6.0	pH 4.0	pH 2.0	pH 1.6	pH 1.4
0	1.00	1.00	1.00	1.00	1.00	1.00
5	1.00	0.98	0.98	0.85	0.74	0.45
10	0.99	0.95	0.93	0.68	0.55	0.10
15	0.99	0.94	0.92	0.60	0.42	0.03
20	0.97	0.93	0.90	0.53	0.37	

* C: observed concentration; C_0: Initial concentration

Generally, atrazine concentration decreased in the following the order: pH 1.4> pH 1.6

> pH 2.0 > pH 4.0 > pH 6.0 > pH 8.0. Figure 27 depicts the relation of the concentration ratio (C/C_0) to the corresponding pH at day 10. A drastic degradation rate change is estimated at about pH 1.75.

In acidic solution in the absence of Fe^0, the major degradant of atrazine was confirmed by LC/MS as hydroxyl atrazine (Figure 28, 29, 30). In LC/MS experiments, 0.25 ml of aliquots were removed at day 0, 7, and 180 and directly injected into the mass spectrometer at the injection rate of 10 μl/min. The atrazine degradation over a long period in this ambient pH was estimated simply by calculation of the ratio (hydroxyl atrazine peak intensity *vs* atrazine peak intensity) in mass spectra and the increased ratio was, 0, 0.2 and 4.0, corresponding to day 0, 7, 180, respectively.

The combined chromatogram (HPLC) of atrazine and its degradants in weak basic solution (80°C, agitation and reflux, 0.05 M Na_2CO_3, pH~10.5) is showed in Figure 31. Atrazine loss was observed, although the degradation mechanism is unclear.

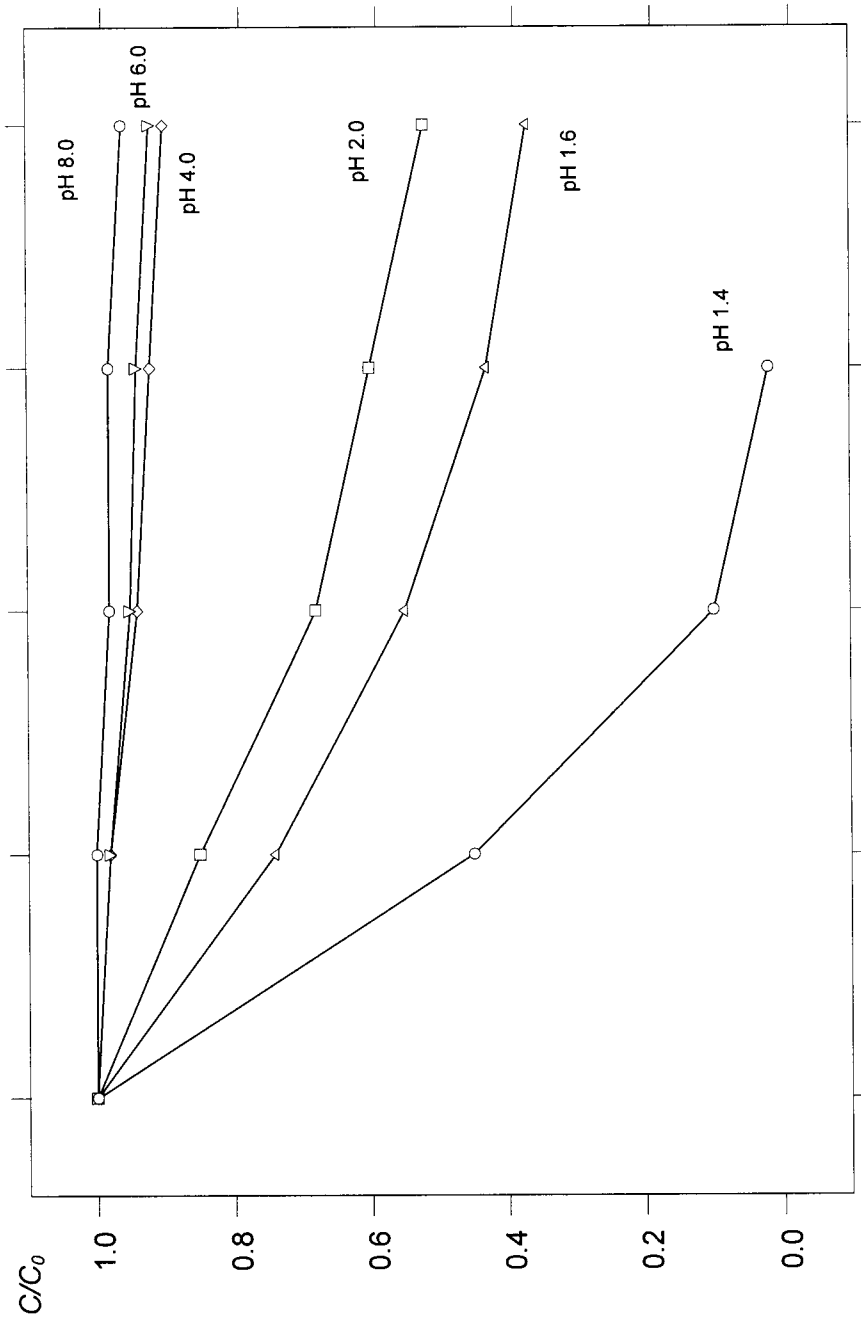


FIGURE 26. Atrazine Stability in Different pH Solution (Calculated as C/C_0). C: Atrazine concentration measured. C_0: Initial concentration of atrazine

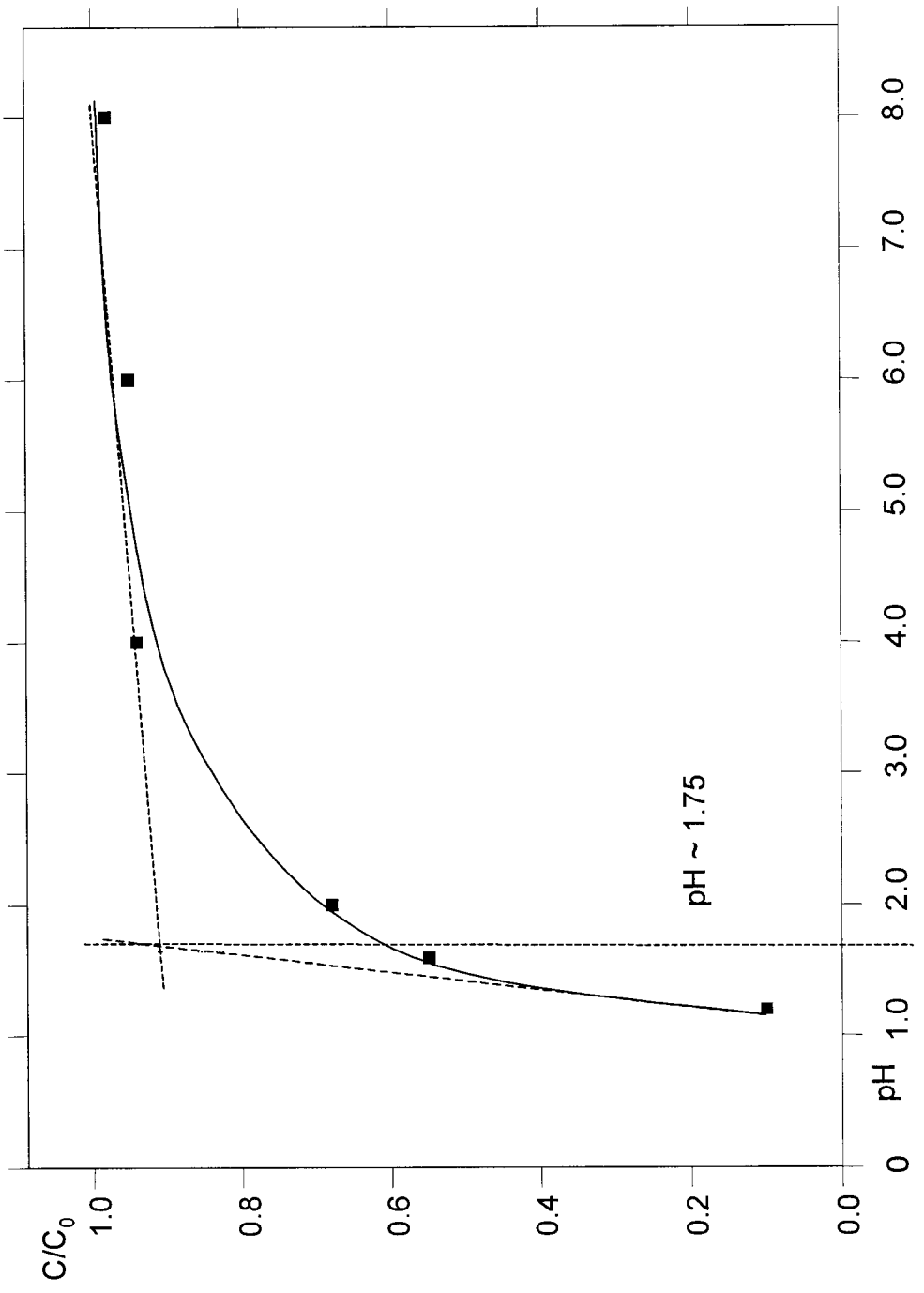


FIGURE 27. Atrazine Concentration Ratio in Different pH Solution on the 10th Day. C: obderved Concentration; C_0: Initial Concentration

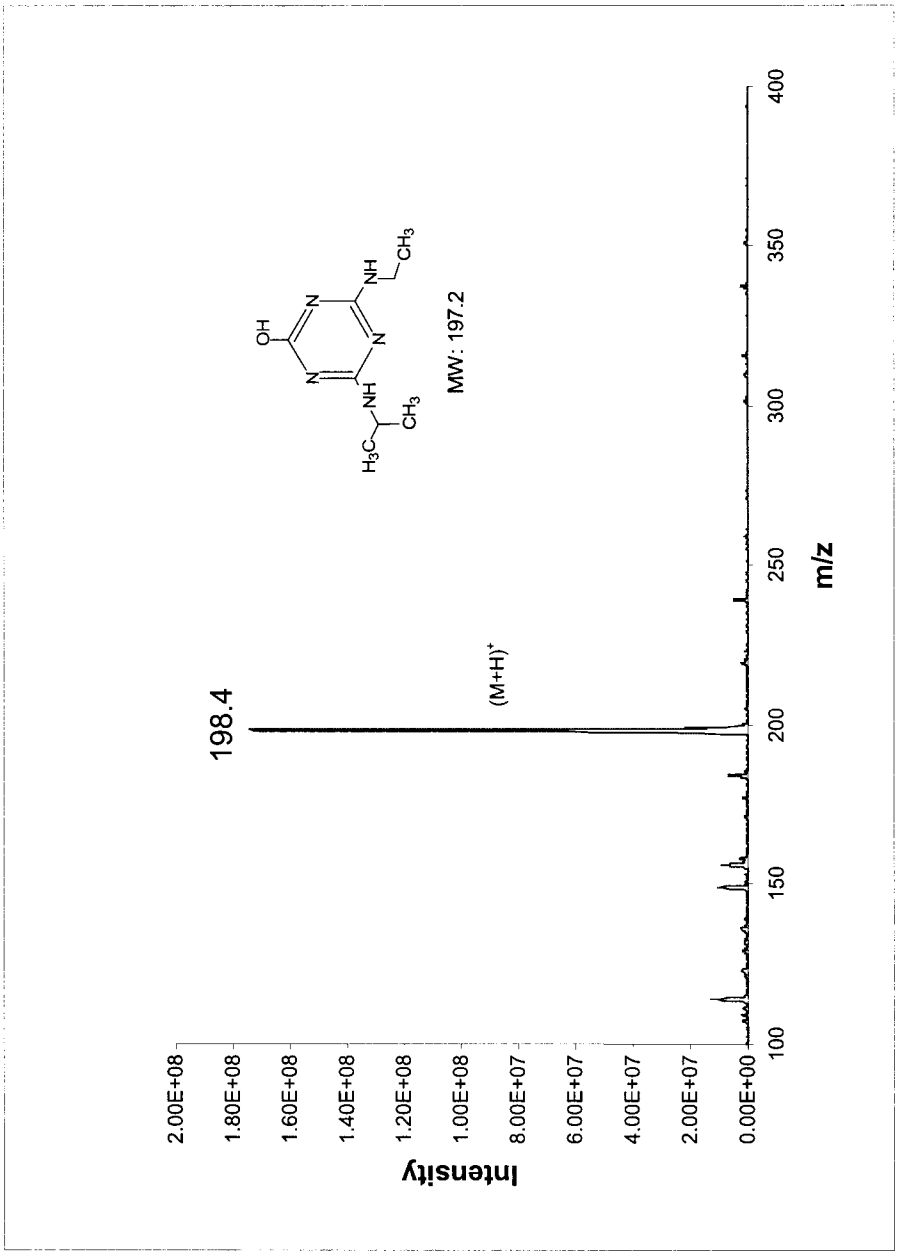


FIGURE 28. LC/MS Spectrum of Hydroxylatrazine in Aqueous Solution

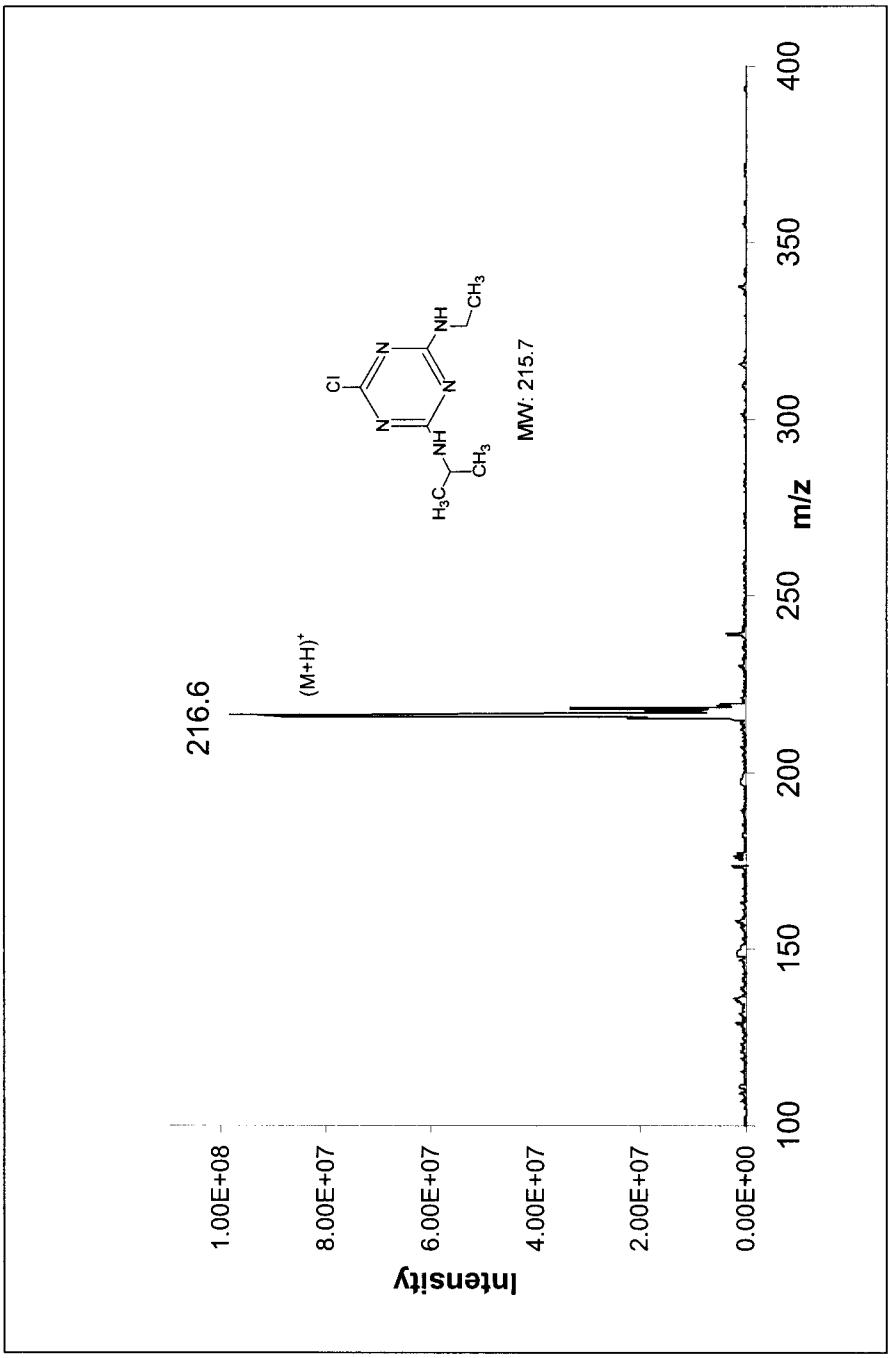


FIGURE 29. LC/MS Spectrum of Atrazine in Aqueous Solution (1) pH=2, at day 1

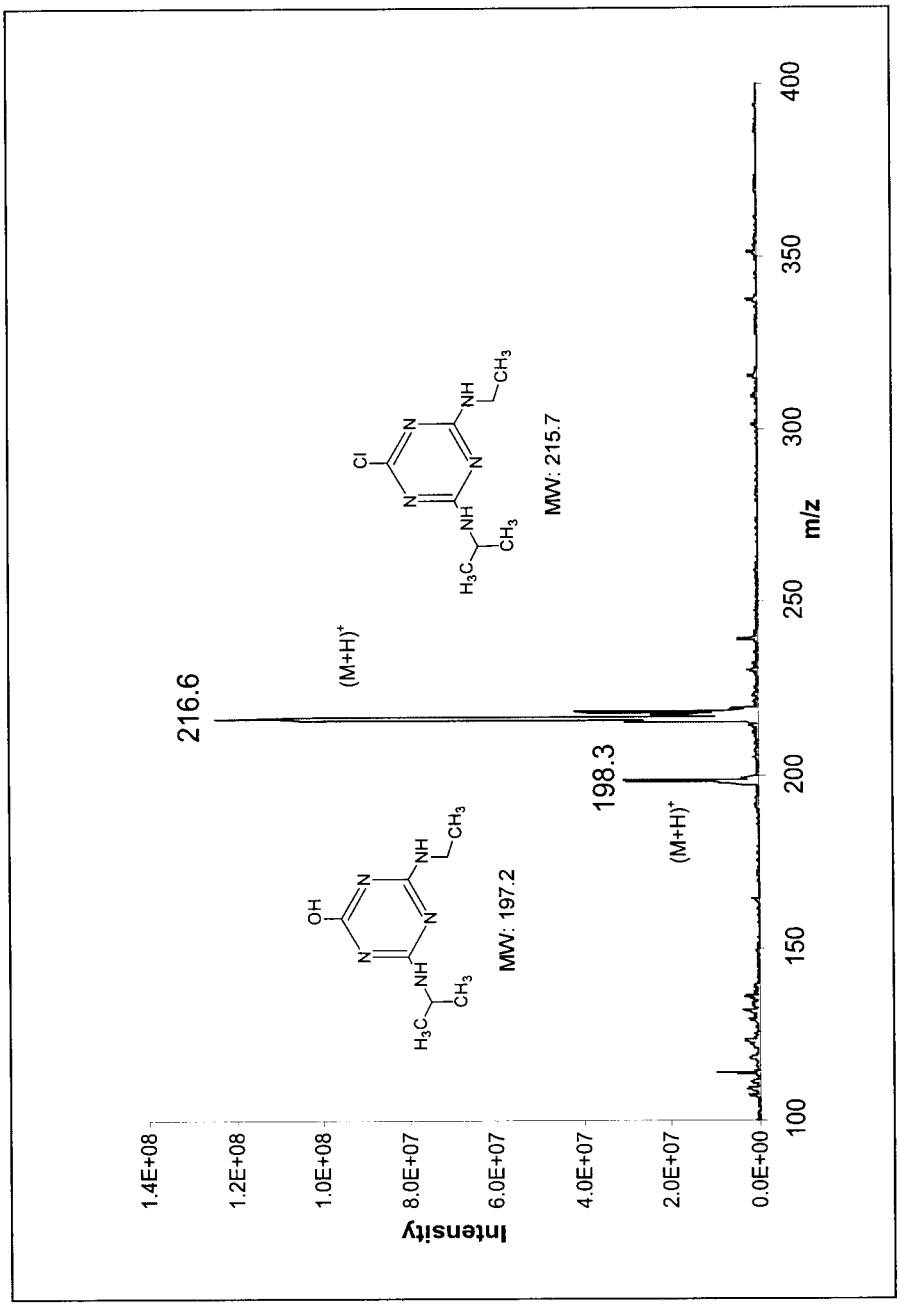


FIGURE 30. LC/MS Spectrum of Atrazine in Aqueous Solution (2) pH=2, after 7 days, the peak of hydroxylatrazine is obvious.

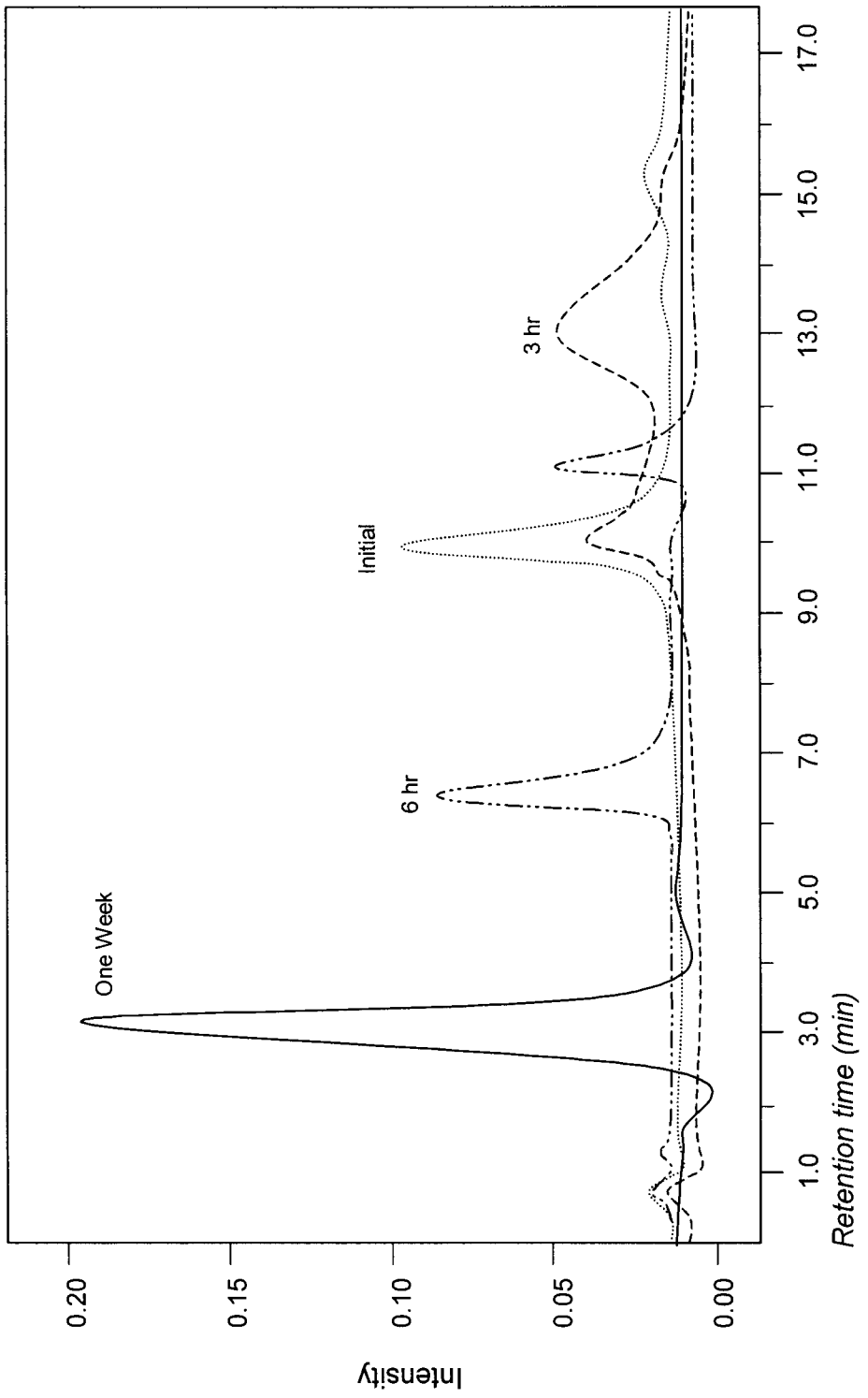


FIGURE 31. Chromatogram (HPLC) of Atrazine in Basic Solution. (atrazine 40 ppm, 80 °C; agitation and reflux; 0.05 M Na_2CO_3, pH~10.5; Mobile: 1:1 of MeOH: H_2O; UV Detector: 200nm; Column: C-18)

3.2. Fe^0 Promoted Reduction

Low atrazine concentration. Reduction of atrazine (40 ppm, with NaBr, 60 ppm) was carried out in acidic solution with 15 g of Fe^0 powder. The solution was sampled at a one-hour intervals and the results are shown in Table 4 and Figure 32.

Strongly acidic solution promoted the removal of atrazine. The rapid loss of atrazine followed the acidic order: pH 1.2 > pH 1.6 >pH 1.8 >pH 2.0 >pH 2.5> pH 3.0> pH 3.5. At pH 1.2, it only took one hour to achieve 97.2% removal of atrazine, and at pH 1.6, 99.4 % atrazine loss was observed while the result in pH 3.5 indicated no significant loss (2.1% at hour 2).

TABLE 4. Atrazine Degradation by Fe^0 at different pH

	Concentation Percentage (C/Co)						
Time(hr)	pH 1.2	pH 1.6	pH 1.8	pH 2.0	pH 2.5	pH 3.0	pH 3.5
	----------	----------	----------	----------	----------	----------	----------
0	100.0	100.0	100.0	100.0	100.0	100.0	100
1	2.8	33.1	55.2	61.2	75.2	85.2	97.9
2		0.6	26.2	40.0	58.6	76.6	97.6
3			3.3	17.2	50.3	71.7	96.6
4				1.4	40.2	65.5	95.2

C: obseved atrazine concentration; C_0: initial atrazine concentration

A plot of relationship between atrazine loss percentage and corresponding pH (at hour 1) is given in Figure 33. The curve turned sharply around pH 1.75.

A typical result of extraction of reaction solution by SPE and subsequent GC/MS is given in mass spectrum (Figure 34), in which, atrazine (m/z 215) and dechlorinated

atrazine (m/z 181) were most frequently detected.

Br^- tracer was also tested by XRF at each sampling and the result showed stable signals with only small random fluctuation (Figure 35).

High atrazine concentration. The reduction of 3.3 g/L of atrazine (67% iso-propanol water solution) with 2.0x10 g of Fe^0 powder was carried out by adding 2 mL of concentrated H_2SO_4. The subsequent TLC separation and GC/MS test found 4 compounds: atrazine, dechlorinated atrazine, methoxy atrazine and iso-propoxy atrazine (Figure 36). Dechlorinated atrazine (Figure 37), methoxyatrazine and isopropoxy atrazine were separated and their UV-Spectra was given in Figure 38. Figure 37 showed the GC/MS spectrum of dechlorinated atrazine separated by TLC, which was recrystallized in methanol. These separated degradation products were used as reference for identification of possible degradants in HPLC test. Further study indicated that both methoxyatrazine and isopropoxyatrazine were caused by the process of sample preparation, in which, methanol or isopropanol was employed as solvent or elution solution of SPEC (Figure 39).

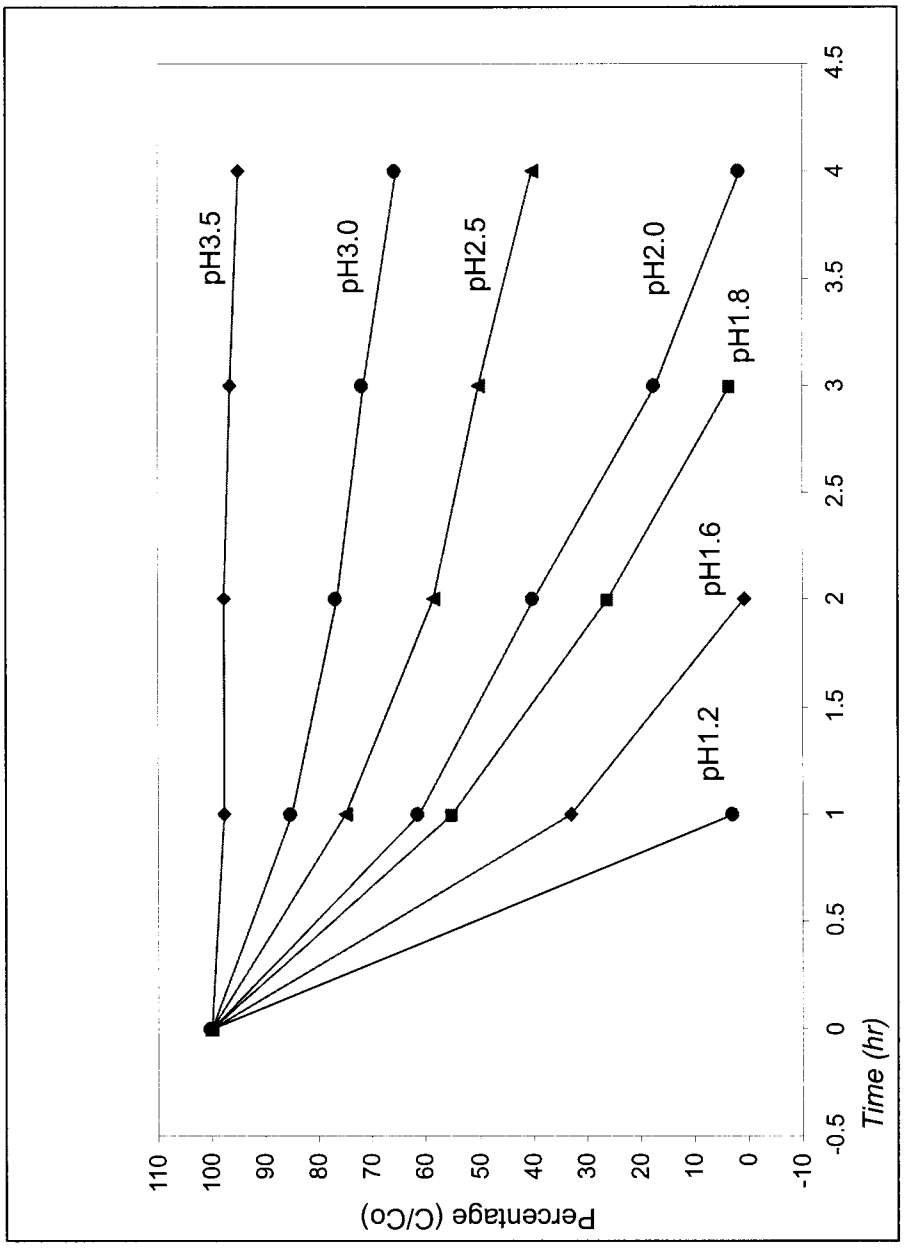


FIGURE 32. Fe^0-Promoted Degradation of Atrazine. (solution contains: atrazine, 40.1ppm; NaBr: 60.0ppm; Fe^0 powder, 15g; pH: adjusted by con H_2SO_4; C_0: initial concentration; C: observed concentration)

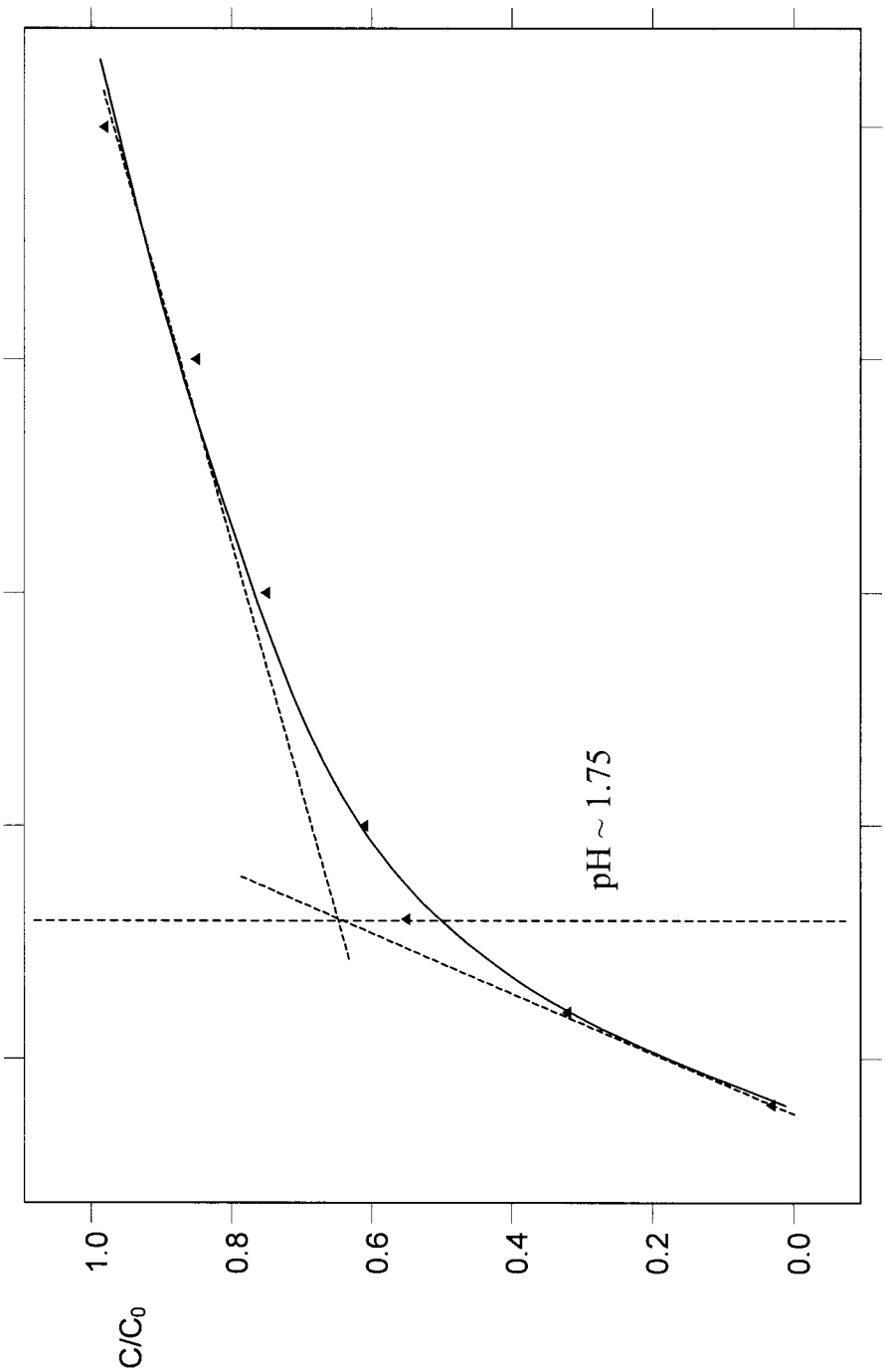


FIGURE 33. Profile of Atrazine Degradation (with Fe^0) at different pH Solution after one hour. (see Figure 32 for details). Degradation curve turns sharply at about pH 1.75

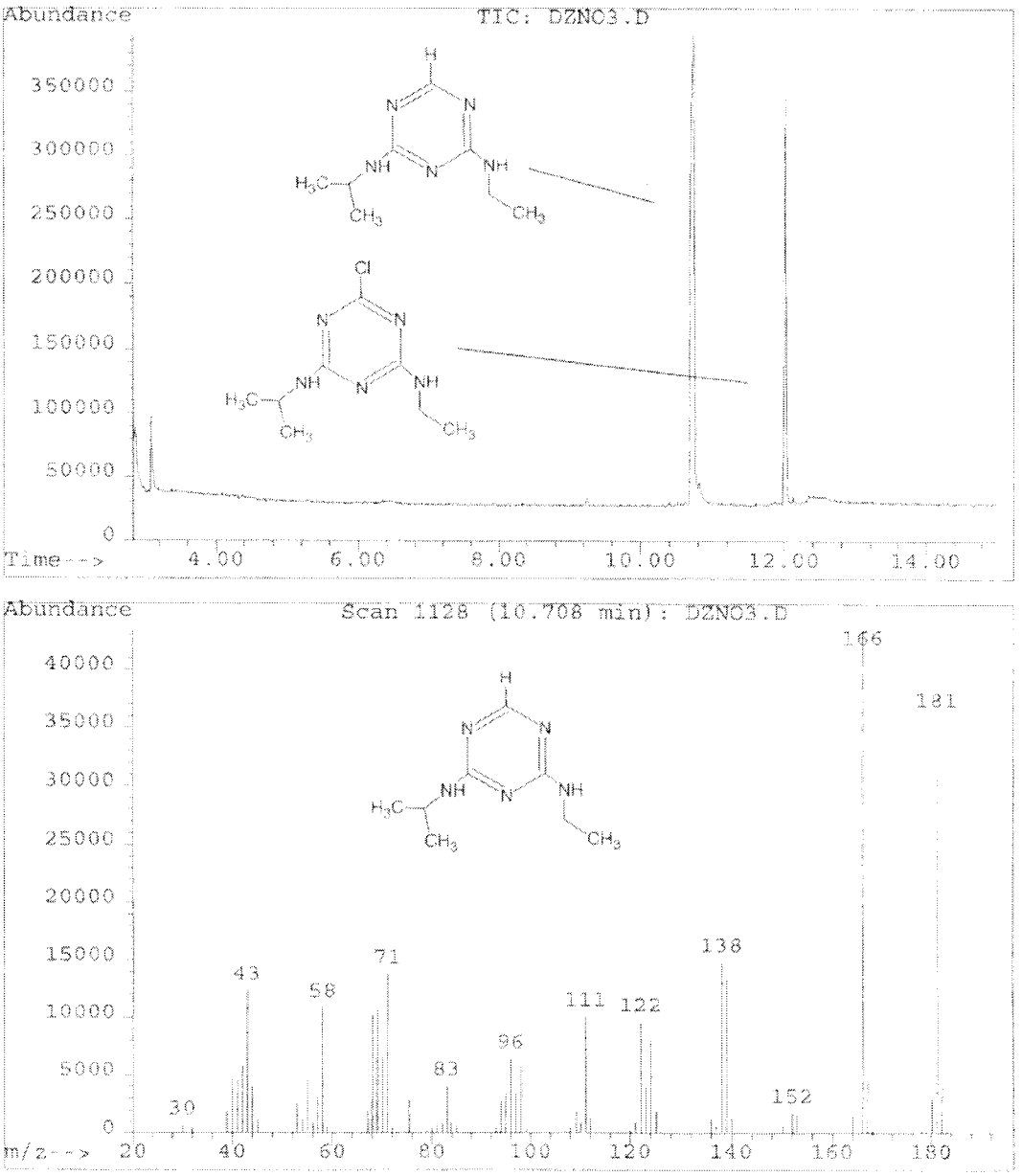


FIGURE 34. GC(MS) Chromatogram of Dechlorinated Atrazine and Atrazine. The sample was extracted from batch reaction (Fe^0-promoted) solution via solid phase extraction and dechlorinated product was identified by mass spectrum

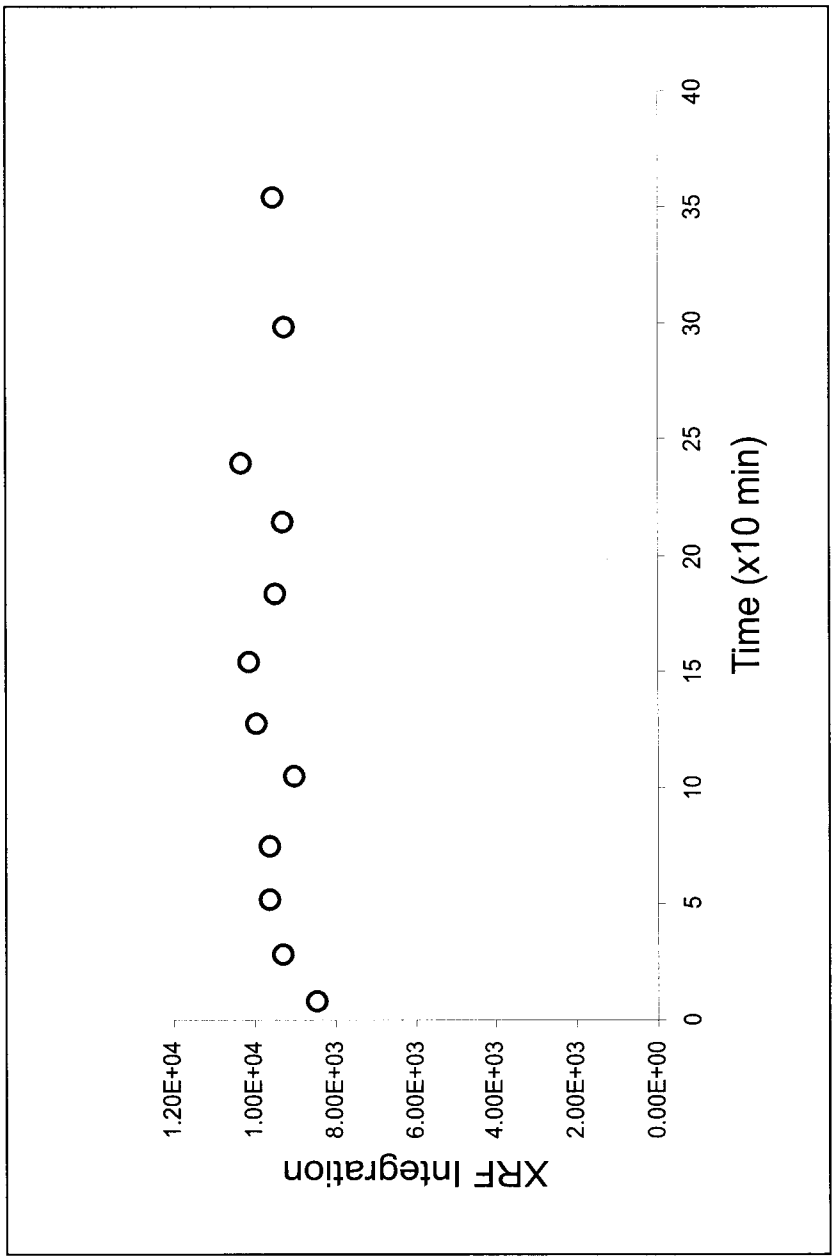


FIGURE 35. Br Determination by XRF during the Batch Reaction. Result indicates that bromide is not involved in the reaction

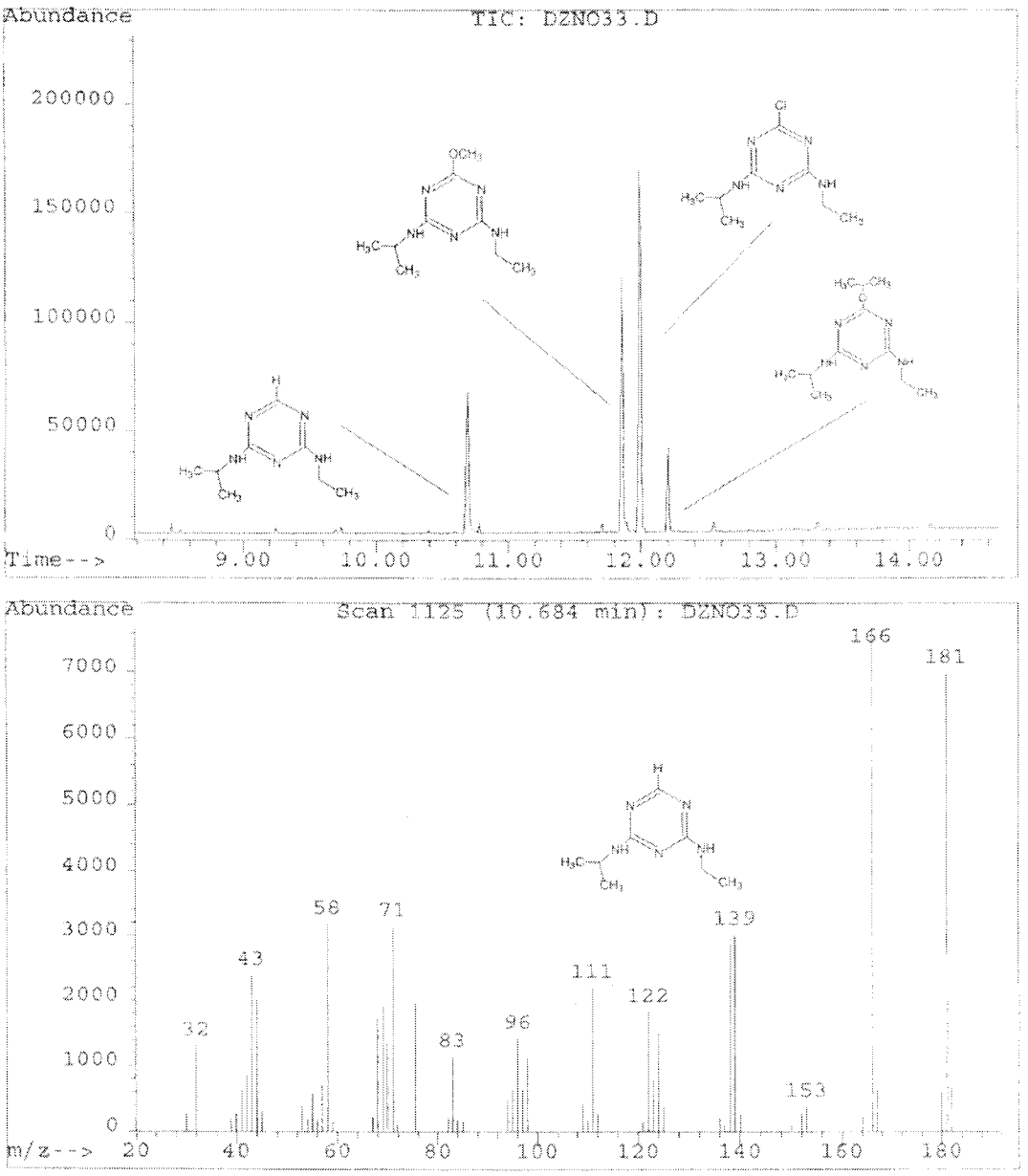


FIGURE 36 GC(MS) Chromatogram of Four compounds. From the reaction solution of Fe-promoted reduction, four compounds were separated and identified: 1. atrazine; 2. dechroinated atrazine; 3. iso-propyl atrazine; 4. methoxyl atrazine.

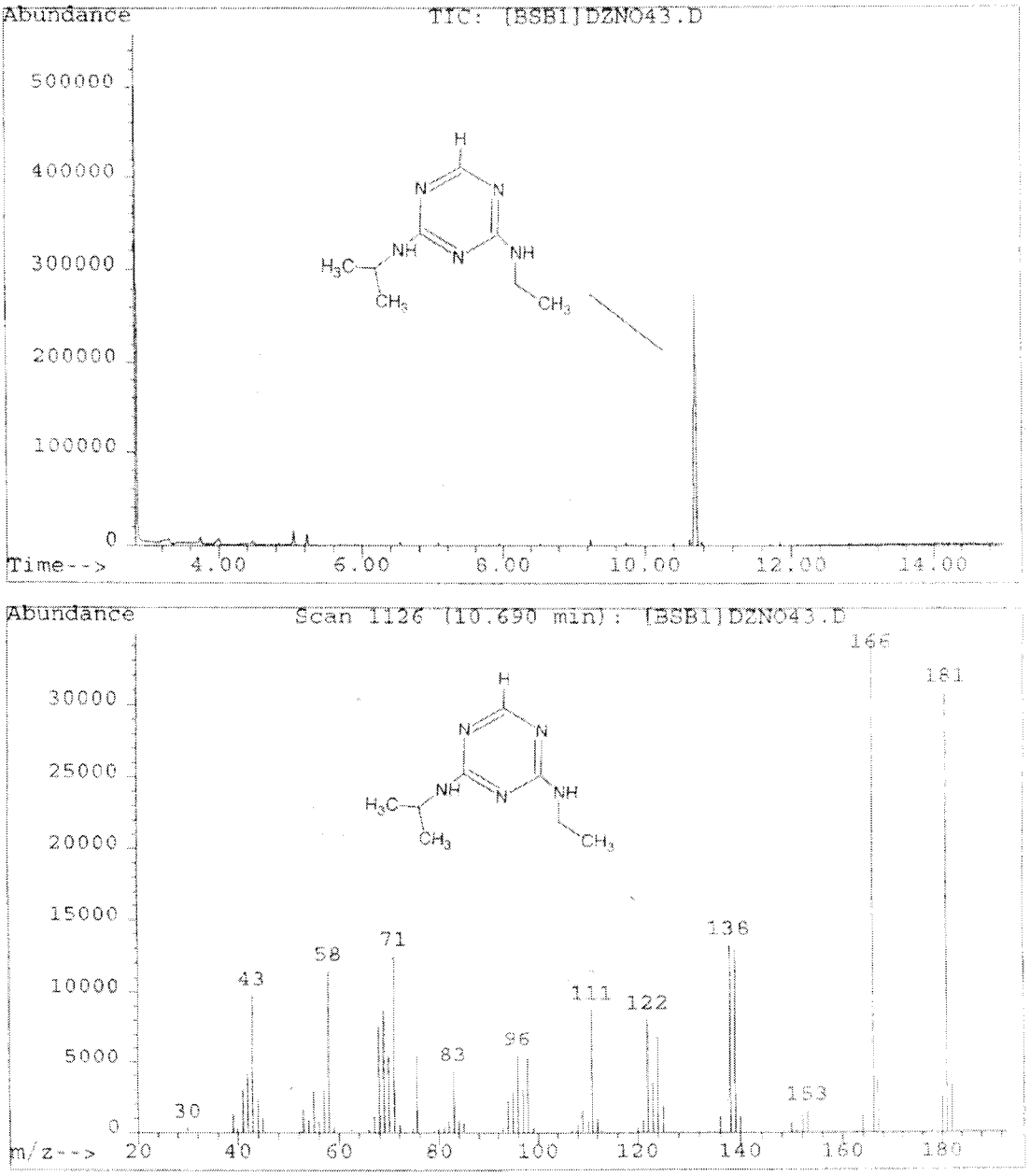


FIGURE 37 GC/MS Spectrum of Dechlorinated Atrazine. The sample was separated via TLC and dechlorinated atrazine was recrystallized.

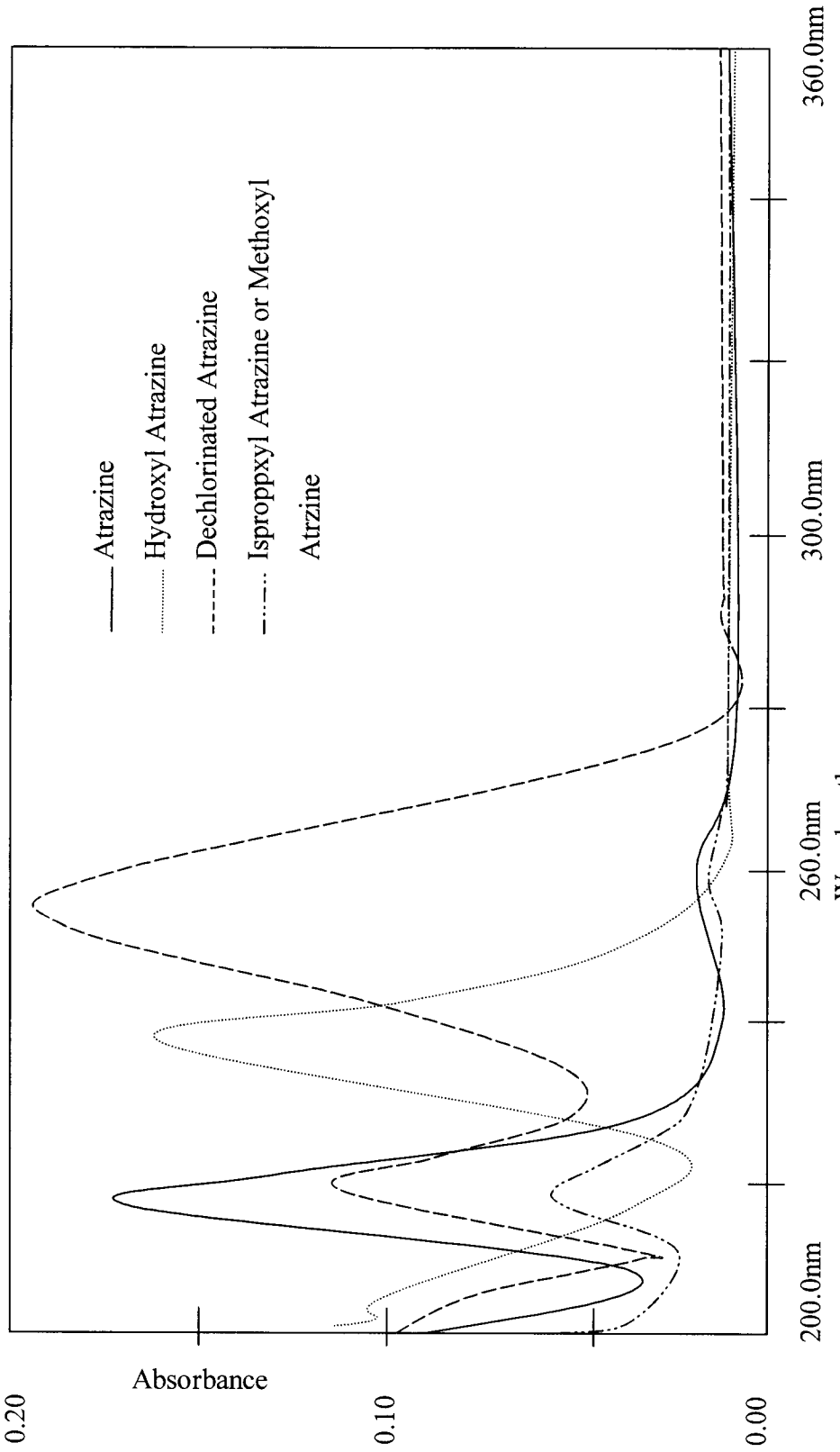


FIGURE 38 UV Spectrum of Atrazine and Degradants.

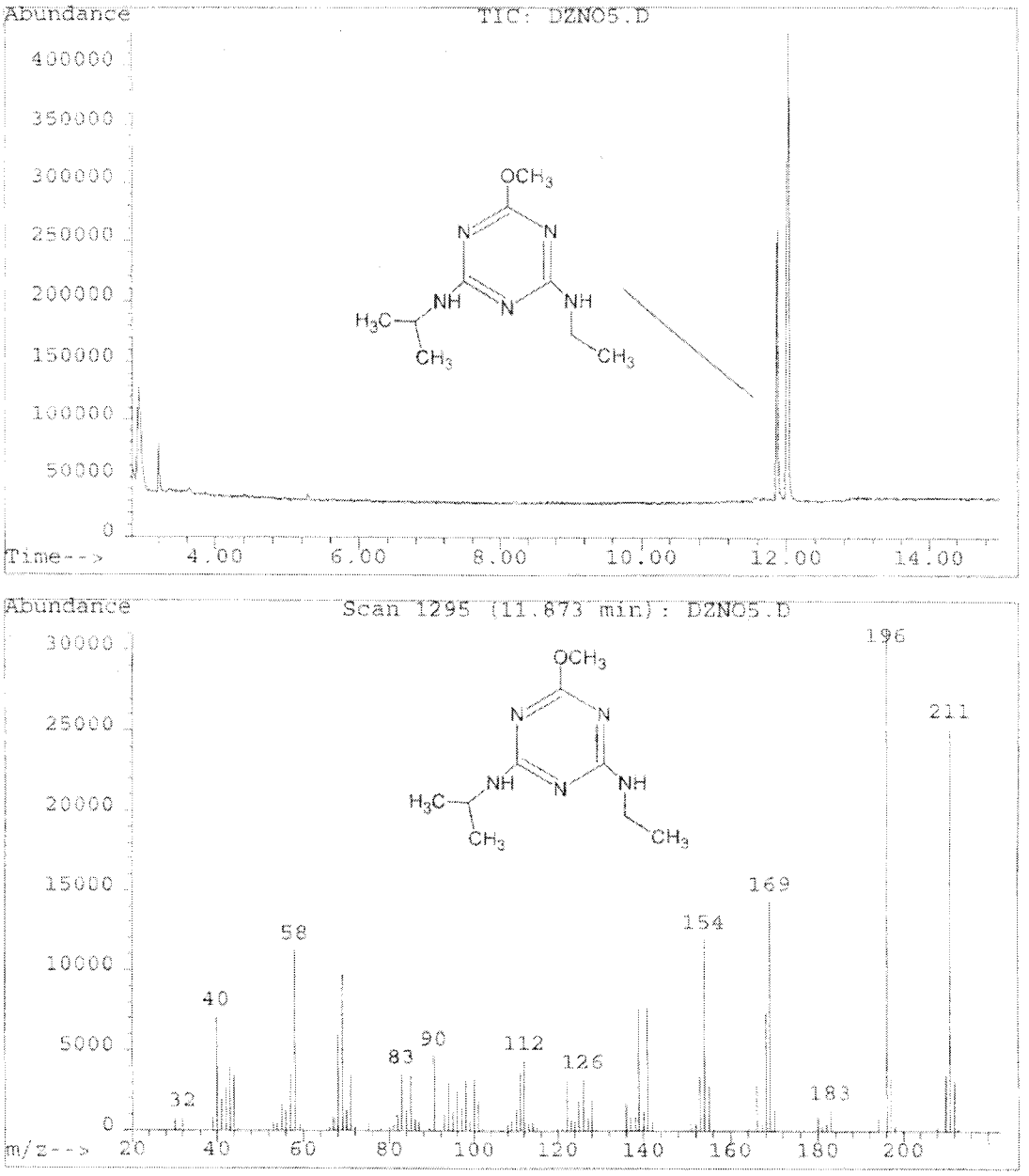


FIGURE 39 GC/MS Spectrum of Methoxyl Atrazine.

3.3. Bromide Tracer Test

In this research, bromide tracer (as NaBr) by XRF measurement was used to monitor the diffusion characteristics of the Fe-sand column. Samples were prepared on the filter paper. The key to good reproducibility of Br^- XRF measurements was an even spread of bromide on the filter paper. While the liquid sample on the filter paper was drying out, a sealed environment was necessary to keep this drying process going slowly and smoothly.

Since the measurement mainly was done on the surface of the paper, the paper sample needed to be very flat when it was fixed on the XRF sample holder. Two pieces of film were necessary.

To obtain a good calculation result, an integrated area (channels) around the central signal channel and the background deduction were necessary. Channels started from 491 to 510 (11.860~12.156 keV), and the background deduction area was a combination of channels 481-490 (11.426~11.455keV) and 511-520 (12.181 ~12.405keV).

The quality of the filter paper showed no significant influence on the XRF measurement. The relationship of XRF signal intensity vs bromide concentration was found to be distinctly and strongly linear (all R^2 values >0.99). The prepared samples were stable at room temperature for at least 24 hours (Figure 40). The linearity of calibration curve could be extended to a large concentration area (Figure 41), ranging from 0 to 0.08 mg/ml (NaBr). The result also showed that the signal noise didn't influence the measurement significantly.

Since the XRF measurement was carried out by counting the impulse intensity over

channels in a certain period (time), its units were different from those of HPLC measurement (column degradation, see section 3.4). To compare XRF result with HPLC data, a normalization of XRF result in order to correlate to the HPLC result was necessary. Following was calculation for normalizing the XRF data:

$$(H_m - H_o) = f\,(X_m - X_o)$$

$$\text{XRF normalized data} = (X - X_o) \times f + H_o$$

H_m: maximum atrazine HPLC measurement (original stock solution).

H_o: blank HPLC measurement.

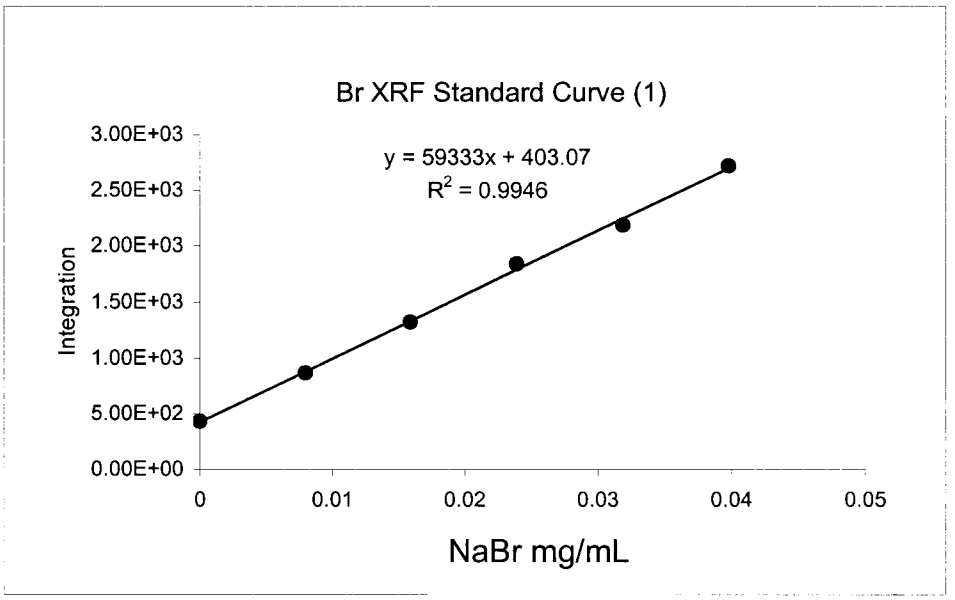
f: Calculation factor.

X_m: maximum XRF measurement (original stock solution).

X_o: XRF blank.

X: actual XRF measurement.

By normalization, XRF data can be shown in the atrazine HPLC plot. The difference between the two curves can be used to calculate the atrazine degradation percentage (See Section 3.4). This was a simplified calculation since the control column (blank) showed no absorption of atrazine on sand in this test. A typical bromide XRF spectrum (three different concentration levels) is shown in Figure 42.



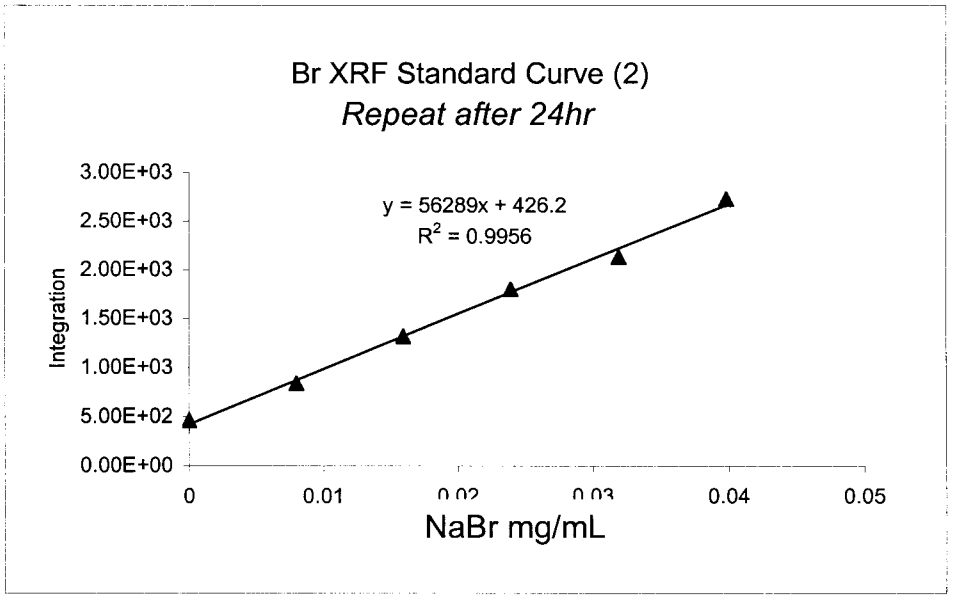


FIGURE 40 Linearity of Br XRF. Both curves show good linearity. The repeated test was done after 24 hr (curve 2) and good reproducibility and stability were observed

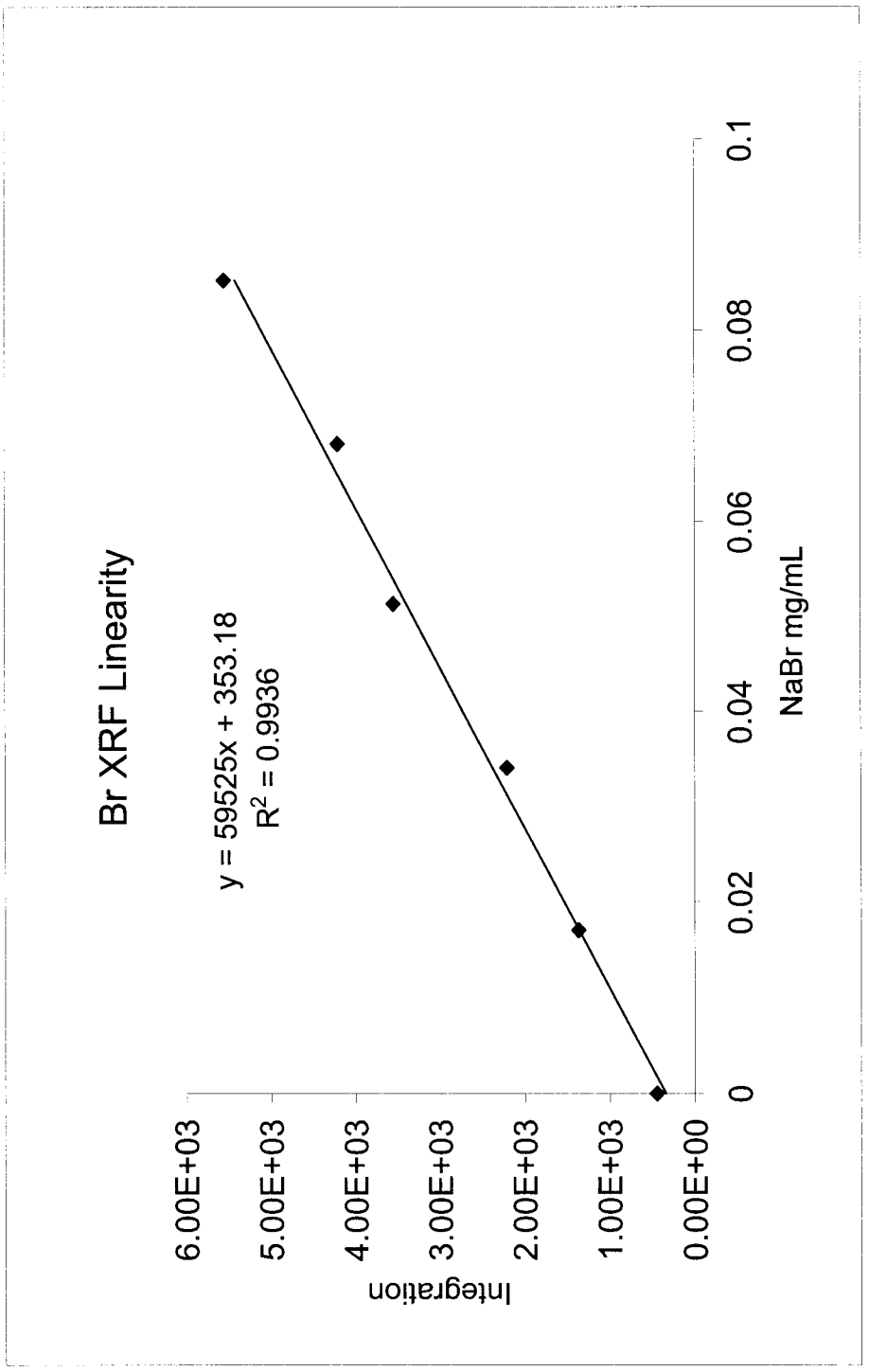


FIGURE 41 Linearity of Br XRF over a Large Concentration Range. The linearity could be observed up to 0.08mg/ml of NaBr.

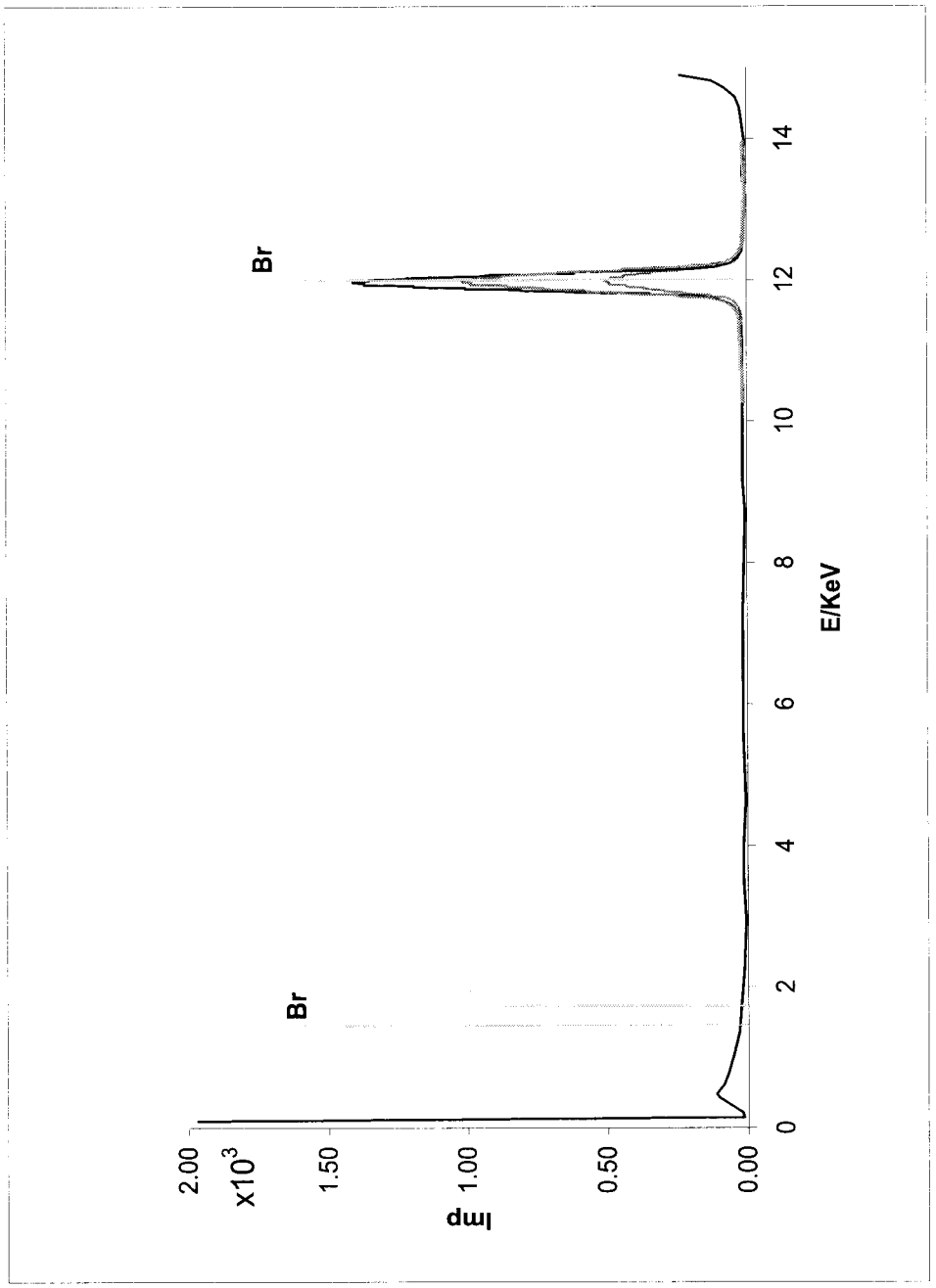


FIGURE 42 Typical Br XRF Spectrum (3 concentration levels)

3.4. Column Degradation

When the acidic atrazine stock solution was pumped into the Fe^0-sand packed column, the atrazine was in a mobile state and was contacting the Fe^0 surface continuously. As the atrazine solution was moving forward, the acidity of the solution dropped quickly and hydrogen gas was produced simultaneously. So the reduction slowed down with the moving of the reaction solution. The reaction mainly took place in the front part of the column.

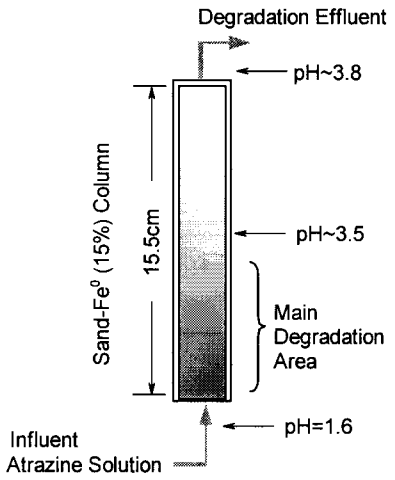


FIGURE 43. A typical column degradation.

Flow Rate: 0.05ml/min

The Fe^0 in the front of the column obviously was depleted first. So for both of the whole column (15.5cm) and the 1/2 column (7.5cm), at similar Fe^0 percentage (w/w), the degradation rates were not significantly influenced by the flow rate if it was below 0.30 ml/min. At the end of the column reaction, usually the effluent pH rose to about pH 3.8 (Figure 43). Figure 44 shows the general calculation of atrazine column degradation using normalization of HPLC data and Br tracer XRF.

With a certain speed and Fe percentage, the initial pH of the influent solution played a very important role, which directly determined the degradation. In this experiment, a maximum degradation of above 60% was observed on the columns with length 7.5, 11.6, and 15.5 cm (Table 5).

In the experiment, when the flow rate was below the 0.05ml/min, the pump would not work properly. So flow rate lower then 0.05 ml/min was not studied. Table 6 shows the influence of flow rate on degradation at initial pH 1.8.

TABLE 5. Average degradation percentage of atrazine (calculated as atrazine loss percentage)

Initial pH	Column Length (x15.5cm)			
	0.25	0.50	0.75	1.00
	----------%----------			
1.60	10.0	62.2	61.2	63.1
1.80	8.0	48.0	50.1	54.3
1.90	2.2	37.8	41.4	39.7
2.00	1.3	29.3	30.0	31.1

Pre-mix. Flow rate: 0.05ml/min,
Percentage: average of 3 individual tests

The overall degradation efficiency is shows in Table 5 and a typical HPLC chromatogram of the column degradation result is shown as in Figure 45.

The combined profile of the interaction of column length, flow rate and degradation is plotted in Figure 46. The profile indicates that when column length was less than 9.3 cm (0.6x15.5 cm), the degradation efficacy dropped sharply and similar scenario was observed when pH > 1.9. Based on the data in Table 6, the standard T-Test for the correlation of different flow rate and degradation was computed (Table 7)

TABLE 6. Influence of flow rate (FR) on atrazine degradation (2 individial tests)

FR (ml/min)	Degradation of Atrazine	
	----------%----------	
0.05	42.7	43.1
0.10	42.8	41.8
0.15	41.6	45.3

Initial pH1.8; Whole column (15.5cm); Mixed *in situ*

The statistics results between each pair of three flow rates fell far short of significance of the general criteria of 0.05 level. So the consequent degradation difference was likely caused by chance.

TABLE 7. T-test for influence of flow rate on degradation

Flow Rate (ml/min)		
0.05 vs 0.10	0.05 vs 0.15	0.10 vs 0.15
T= 0.72	0.75	0.38

Customary Level: 0.05; Critical Value: 4.30

For a clear understanding of this interaction, more data and tests were needed. However, this test indicated that at flow rate had no significant influence on the degradation if it was low.

FIGURE 44. The process of XRF Normalization and Atrazine Degradation Calculation.

C_0: Concentration of the stock solution. NaBr concentration has been normalized to fit the plot of the atrazine concentration.

C_0': Mobile concentration of NaBr(XRF); after normalization, it indicates the process of stock solution (atrazine) diffusion in the column

C: Mobile atrazine concentration (HPLC).

The actual degration of atrazine can be calculated as:

$$\text{Degradation Percentage} = \frac{C_0' - C}{C_0'} \times 100$$

Normally, it would take a long time for C_0' to achieve C_0 due to a very low flow rate of mobile stock solution in the column.

Data in this plot were acquired under condition:

Starting pH 1.75

Flowrate 0.05 ml/min.

1/2 column

15% of Fe^0 (w/w) in sand

Stock solution: Atrazine 40ppm

NaBr 60ppm

Sampling: collect every 5mL elute

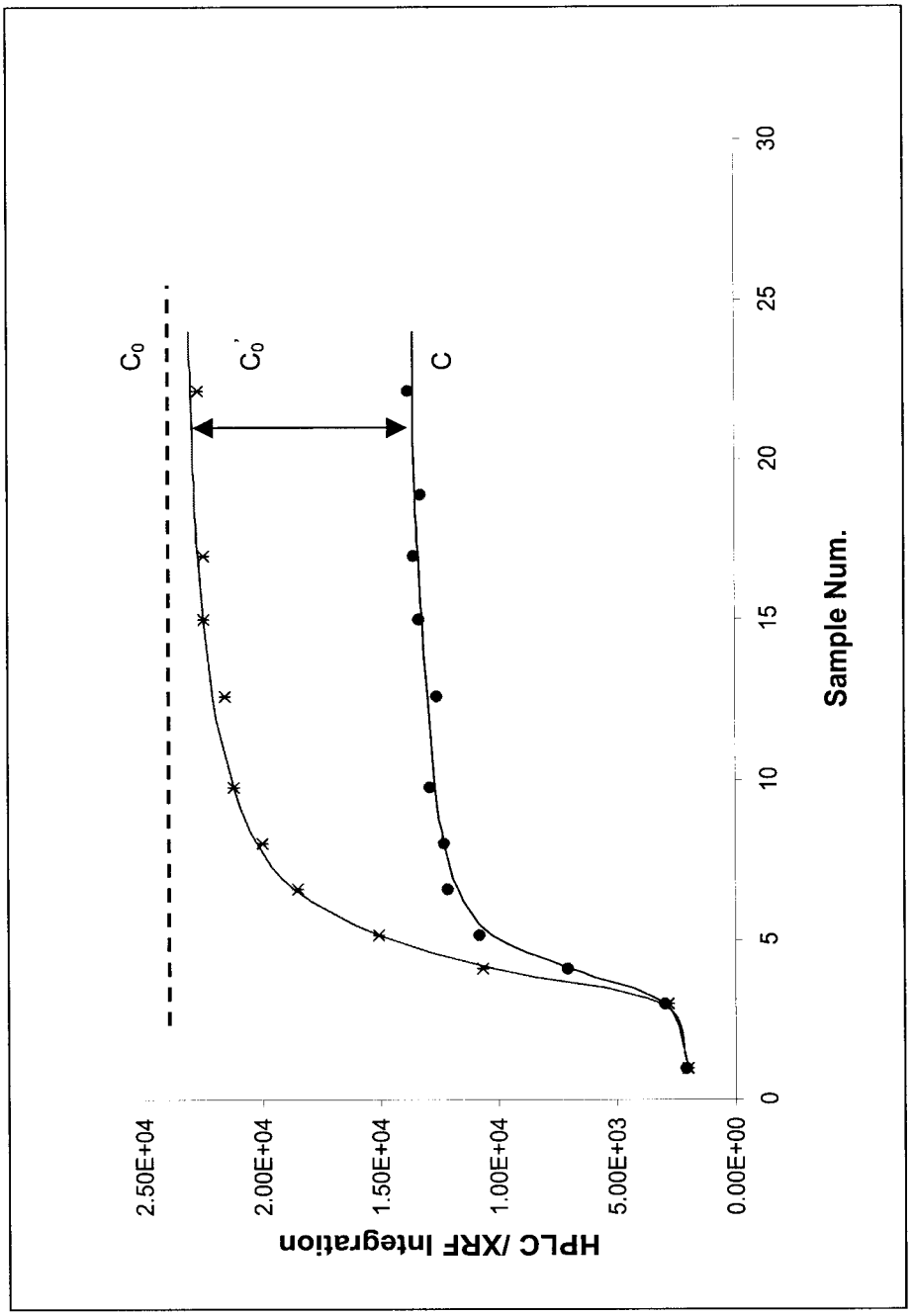


FIGURE 44. The process of XRF Normalization and Atrazine Degradation Calculation

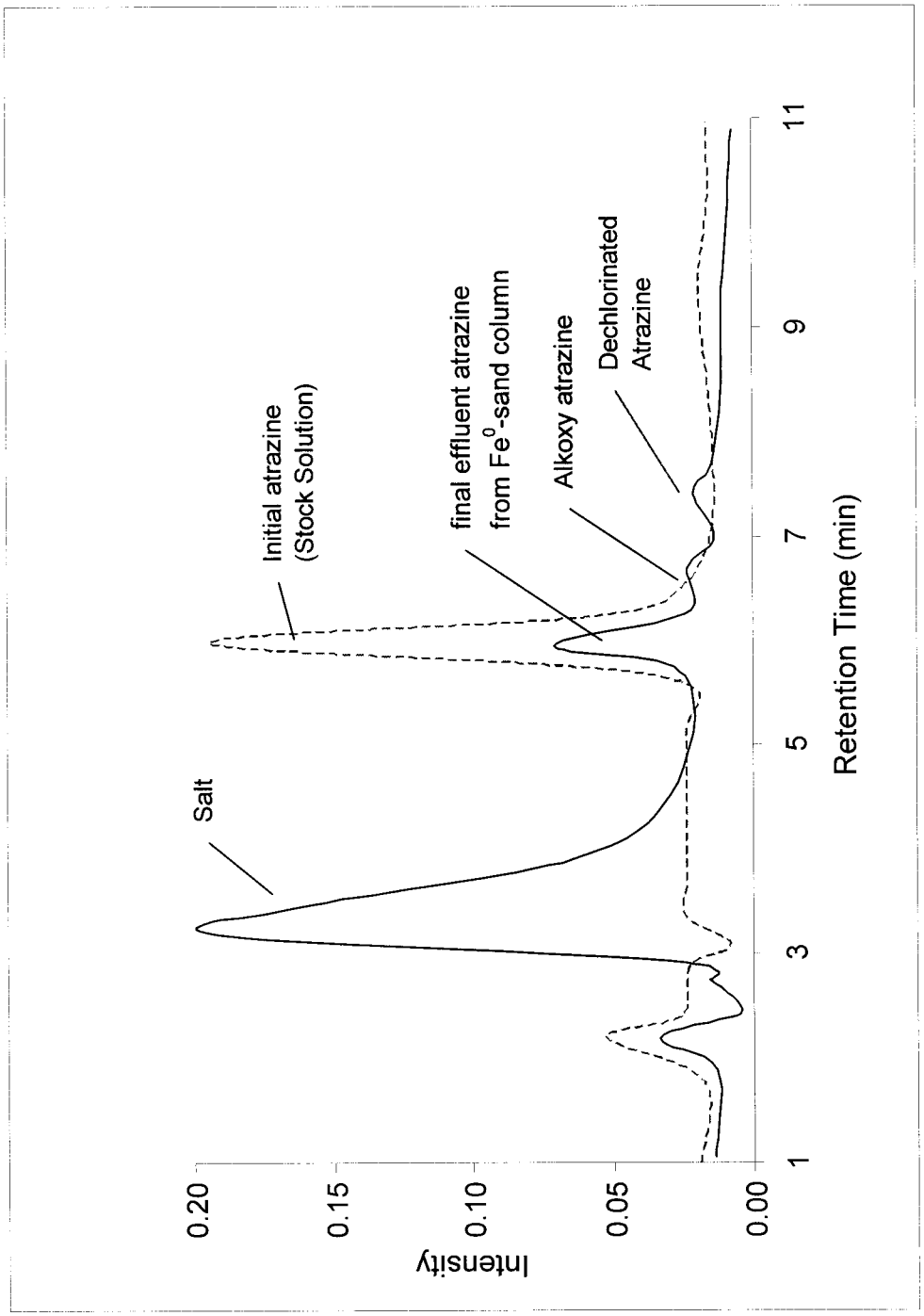


FIGURE 45 A Typical HPLC Chromatogram of Column Degradation

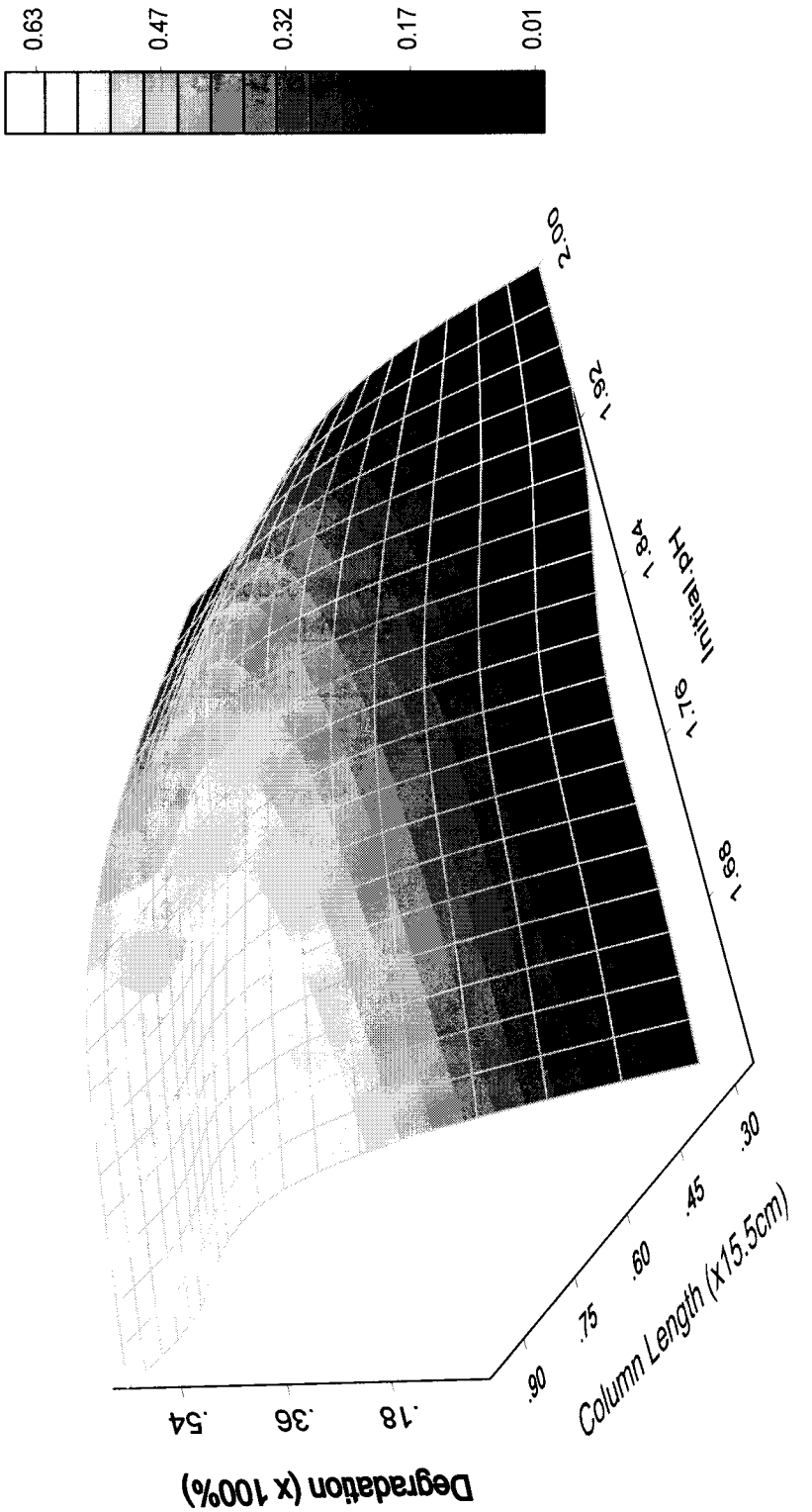


FIGURE 46. Column Degradation Efficiency. (Flow rate; 0.05ml/min, pre-mixed)

4. DISCUSSION

4.1. Protonation of Atrazine

Atrazine was not stable in low pH water solution, especially when pH is lower than 2.0. This was very obvious when atrazine stock solution was prepared in low pH solution and stored after a week. It was quite stable in weak acidic, neutral and weak basic solution. The observed loss of atrazine in acidic solution was due to the hydrolysis. It was consistent with the results by Plust *et al.* (1981) in a study of acid-catalyzed hydrolysis of atrazine (Table 8)

TABLE 8* . Pseudo-First-Order Rate Constant for the Hydrolysis of Atrazine in Aqueous Solution

at 25.00 ± 0.05 °C		at 39.90 ± 0.05 °C	
pH	$10^6 k'$, s^{-1}	pH	$10^6 k'$, s^{-1}
0.46	4.6	0.4	19.9
0.74	2.78	0.4	16.4
1	2.36	0.48	22
1.07	1.6	0.7	12.7
1.3	1.58	0.7	11.6
1.36	1.08	0.88	11.8
1.66	0.704	0.97	9.92
1.68	0.699	1	9.75
2	0.578	1	8.57
2.06	0.497	1	8.5
2.2	0.438	1.13	8.39
3.1	0.121	1.36	5.83
4	0.0329	1.58	4.08
11.1	0.099	1.6	4.41
11.9	0.529	1.61	3.61
12.9	4.29	2	1.77
		2.1	1.84
		2.6	0.85
		2.6	0.76
		3.1	0.26
		4	0.165

* Plust *et al.* 1981

Armstrong *et al.* (1967) suggested that in the process of hydrolysis of atrazine, the protonation of atrazine was the rate-limiting step. In later research, Li *et al.* (1972) and Plust *et al.* (1981) noticed remarkably larger rate constant values of hydrolysis at very low pH, and thus suggested an additional process of diprotonating atrazine might account for a much more rapid hydrolysis at the low pH. In our experiment, a pH-degradation profile showed a similar trend (Figure 27).

Based on spectrophotometric result of titration of atrazine with acid, Plust *et al.* (1981) further reported that monoprotonation of atrazine was indeed an equilibrium of three monoprotonated forms, in which, the proton attached to the ring nitrogens. Thus the measured pKa value (1.62± 0.03 at 20± 2°C) would be a composite related to three heterocyclic nitrogens. It is unlikely that these three individual pKas are equally weighted and also unlikely that hydrolysis occurrs solely from monoprotonation on any single nitrogen on the triazine ring.

Hydrolysis of atrazine at room temperature without a catalyst, like a proton, was rather difficult. The degradation of atrazine in 0.05 M sodium carbonate solution (~pH 10.5) proceeded relatively fast at 80 °C with agitation, with 100% degradation at day 7. The control test at room temperature showed no remarkable change of atrazine concentration. In the HPLC chromatogram (Figure 31), the final degradant appeared with a retention time of about 3 min, compared with atrazine, 10 min. This is consistent with the polar characteristics of hydrolysis product, hydroxyl atrazine. The reported pKa of

hydroxyatrazine is 5.15 (Lerch *et al.*, 1994).

4.2. Fe^0 Promoted Reduction

Acid catalyzed degradation of atrazine took a much longer time when compared with the zero-valent iron promoted reduction. Table 3 showed that at pH 1.6, without Fe^0, 63% of atrazine was lost after 20 days. However, it took less than 1 hour to achieve a similar result in the presence of Fe^0 powder at the same pH.

Like hydrolysis of atrazine, protonation was also critical in Fe^0 promoted reduction of atrazine. However, the protonation might not be simply regarded as a catalysis since the proton was involved in the substitution of chlorine on the aromatic ring via oxidation/reduction process. The detailed mechanism is discussed later. It is very possible that diprotonation could make a substantial contribution to the reduction in strongly acidic condition since a doubly charged (positive) triazine ring would be more susceptible to reduction.

The purpose of these experiments were to get a clear understanding of the zero valent iron reduction of atrazine, which was helpful for designing and conducting the column degradation. Reduction of atrazine was carried out in acidic solution with Fe^0 powder and tracer bromide (NaBr) was also added for the evaluation. Under the protection of N_2 blanket, the possible oxidation of Fe^0 could be diminished greatly and the reduction proceeded in an "anoxic" condition. This was proper since in contaminated water in the

environment, anoxic conditions commonly develop. Due to agitation, it was assumed that the mass transfer of atrazine to the iron surface was not rate limiting.

Low ambient pH obviously facilitates the atrazine reduction, especially with pH values below 1.8. At pH 1.2, atrazine loss was up to 97.2% (Table 4), and this extremely facile reaction might be attributed to diprotonation of atrazine. It is widely believed that protonation is the first step to atrazine degradation by Fe^0 (Dombek *et al.*, 2001; Monson *et al.*, 1998; Singh *et al.*, 1998).

An atrazine concentration ratio-pH profile shows that the degradation rate changes at about pH 1.75 (Figure 33), which is very similar to the profile of hydrolysis-pH as described in Figure 27. The stark similarity implies some mechanistic consistency between hydrolysis and reduction of atrazine. The mechanism is discussed later.

Br^- tracer was also tested at each sampling and the result shows stable signals with only small random fluctuation (Figure 35), which indicates that bromide was nonreactive in the reaction and was a conservative tracer.

The products from the high atrazine concentration reduction were analyzed via SPE, TLC and GC/MS and will be discussed in the mechanism section.

4.3. Column Degradation and Bromide Tracer

Column degradation could be regarded as an extension from Fe^0 promoted solution reduction. The purpose of column study was to investigate the feasibility of using

Fe^0-mended soil as a cost effective practice for on-site decontamination in atrazine contaminated fields

Since the Fe^0 and sand was well mixed before and during the column packing process, it was assumed that atrazine would have access to all available iron sites as the solution feeding in and thus the mass transfer was not the rate-limiting step. Obviously, acidity was a key factor to affect the overall removal efficiency (Table 5). A difference about 2 units of pH value was observed between influent and effluent solution, which indicated that the most degradation occurred at the front part of the column. 15% of Fe^0 (w/w) in sand column was used and chance for atrazine to access the reductive iron surface was adjusted by changing the length of the column and flow rate. The effect of column length and flow rate on overall degradation rate was less than ambient pH if the column was longer than 7.8 cm and flow rate was less than 0.15 ml/min. A better removal rate could be achieved if the pH of the feeding solution was controlled. However, buffer solution was not used in column degradation since a weak acid might improve the degradation, which was not within the scope of this study.

A simple calculation of atrazine removal percentage was provided in the results section (see Figure 44). However, if real soil was used instead of sand to pack the column, the adsorption of atrazine on soil organic substances should not be ignored. In that case, a control column would be employed to evaluate the adsorption.

Also, a widely used calculation, in which the degree of nutrient attenuation in a field

was qualified with respect to Br^- tracer (Casey *et al.*, 2001), could be adopted:

$$\% \text{ attenuation} = [1- (\text{observed ratio/initial ratio})]x\ 100\%$$

$$\text{ratio: (concetration of } NO_3^- \text{ or } PO_4^{3-}\text{) / (concentration of } Br^-\text{)}$$

In the above equation, the initial ratio was measured at the inlet of amended surface water while observed ratio measured at a given measurement site. This equation could be modified for qualifying the atrazine removal degree (%) but is more proper for a field study.

The advantages of determination of bromide tracer by XRF are: (1) easy preparation of samples (2) It is a sensitive measurement. For a very low limit of Br measurement, two pieces of sample paper might be employed and a longer XRF counting time could be adopted. (3) Br atom has its own characteristic XRF wavelength (channels) and thus is seldom influenced by other elements, so a good selectivity is expected (Figure 42). (4) Measurement is reproducible. (5) It is proper to deal with soil sample since natural content of bromide is very low in soil and Br^- interaction with soil constituents is minimal.

4.4. Proposed Mechanism and Degradants

4.4.1. Dechlorinated Atrazine

Low pH significantly accelerates the degradation both with Fe^0 and without Fe^0. The curves (C/C_0 to pH) turned at about pH 1.75, very close to the reported atrazine pKa (1.7,

very weak base, Agdi *et al.*,2000). When solution pH is lower than pH 1.7 the equilibrium favors protonation of the triazine ring. Plust *et al.* (1981) reported diprotonation and monoprotonation in low pH (pH<2), and difference among three heterocyclic nitrogens, which implied a high pKa' value at ring nitrogen N5. Higuera *et al.* (1999) described a pKa value of simazine on ring nitrogen N5 of 1.7.

This protonation is reasonable since nonbonding electrons of the three heterocyclic nitrogen atoms in the triazine ring are in sp^2 hybridized and have no contribution to the ring. Instead, the electronegativity of the nitrogen pulls the electrons in the ring system toward the nitrogen atoms themselves, which, in turn, makes the triazine ring extremely electron-deficient.

On the other hand, due to the increased negative characteristic of ring nitrogen atoms, it is easy for them to be protonated, if ambient acidity is enough. The protonation make the triazine ring system more positive, which would, in turn, facilitate the uptake of electrons from the iron or other electron-donors; the reaction is followed by substitution of chlorine with a proton.

The detailed mechanism of this type reduction is not very clear. Roberts *et.al.*(1996) proposed a pathway for reduction of trans-dichloroethylene by zero-valent metals (see Introduction), which was involved in negative radical intermediate products. Their later research (Arnold *et al.*, 2000) indicated adsorption of organic contaminants on Fe^0 surface as the rate-limiting step of reduction. Thus a metal (Fe^0) surface-promoted reduction

mechanism was suggested. However, for atrazine reduction, this pre-adsorption on the iron surface might not be so critical since it lacks an electron-rich π bond to form the important π-bonding with the iron surface. It is likely that the reduction of atrazine in the presence of Fe^0 goes through a process involving radical intermediates. Skopalová *et al.*(1995), using pulse voltammetry to study reduction of s-triazine herbicides, confirmed that only the protonated form of s-trazine herbicides is reduced. They observed four electrons per reactant in the reduction. Similar results were found by Higuera *et al.*(1999) in the study of simazine reduction using polarography and by Pospisil *et al.* (1995) and Ignjatovic *et al.* (1993) in the study of electrochemical reduction of terbutylazine and atrazine,

Many proposed reduction mechanisms of s-triazine herbicides have been proposed based on the electron process on the mercury electrode, but the similarity of the electron transfer in redox process would be helpful in elucidation of the reduction mechanism of atrazine by Fe^0.

Figure 47 shows the proposed mechanism for reduction of atrazine by Fe^0 at pH<pKa (1.7). The important intermediate is possibly a dechlorinated radical. In acidic solution, protonation probably occurrs first to activate the triazine ring. Fe^0 donates two electrons and is oxidized to Fe^{2+} ion. Atrazine acceptes the two electrons to form a radical (III); this is a very unstable and is followed by chlorine bond cleavage (III, IV); the proton at N1 or N3 shifts to the carbon that was previously bonded to chlorine (IV, V); the stable dechlorinated product VI is formed after deprotonation step (V). The dechlorinated

atrazine was separated via TLC from thr reaction mixture and is identified by GC/MS (Figure 34, 37).

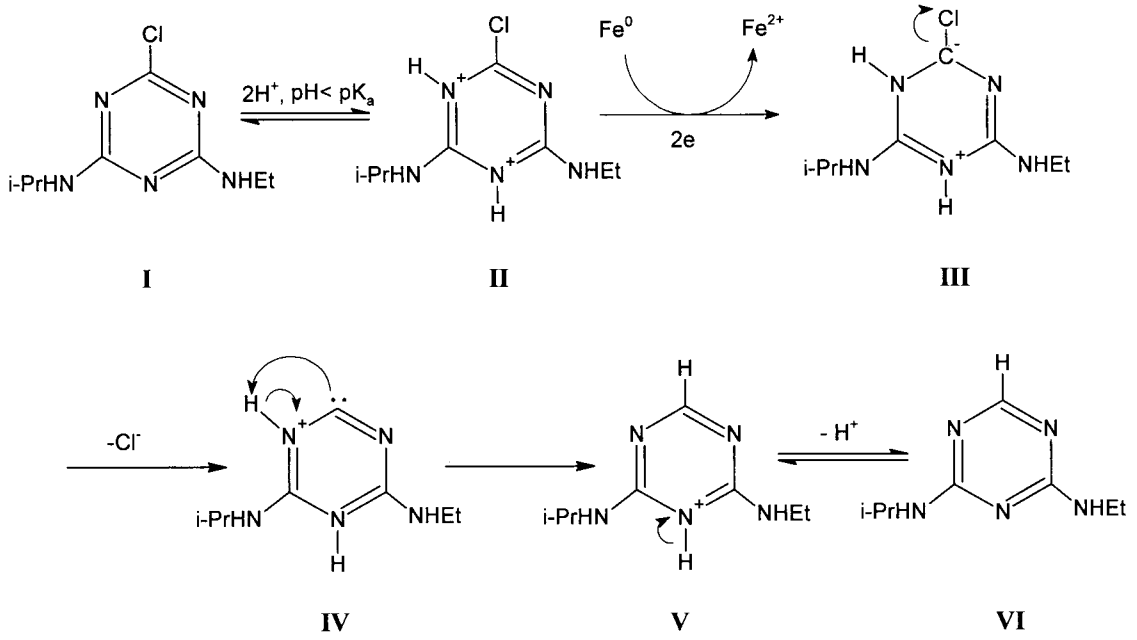


FIGURE 47. A proposed pathway of atrazine degradation at pH< pKa

A similar mechanism occurred when this degradation reaction proceeded at ambient pH > pKa, and the process was preceded by monoprotonation.

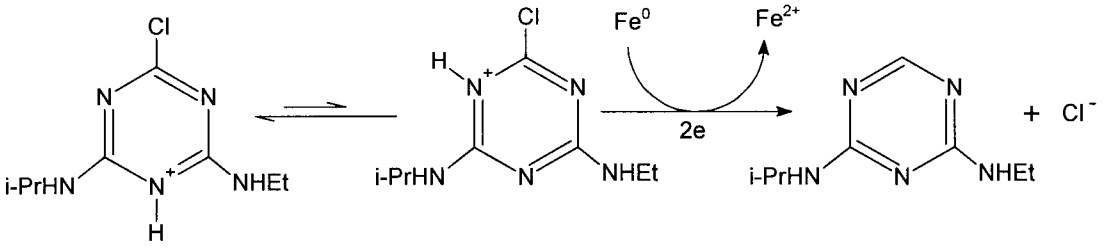


FIGURE 48. Proposed mechanism of atrazine degradation via monoprotonation.

In many cases studied, dechlorinated atrazine was the major product observed. Under reductive conditions, atrazine loss could probably account for the dechlorinated atrazine formation. In the high atrazine concentration degradation study, the reaction solution was concentrated by vacuum evaporation (with liquid N_2 bath trap). Then the concentrated solution was subjected to TLC separation. The formular mass of dechlorinated atrazine was confirmed by GC/MS. The dechlorinated atrazine was obtained and identified through TLC separation. However, the exact estimation of the quantity of dechlorinated degradant was difficult since dechlorinated atrazine continues to degrade. Usually, at the end of the reaction, both atrazine and dechlorinated atrazine peaks in the HPLC chromatogram were very weak. This was also true for the GC/MS result.

Heguera *et al.* (1999) and Galvín *et al.* (2002) observed further hydrogenation of the dechlorinated triazine ring via polarographic and voltammetric studies. It was expected that a similar second two-electron reduction of dechlorinated atrazine in the 1-2 or 2-3 position proceeded also in Fe^0 -promoted reduction (Figure 49).

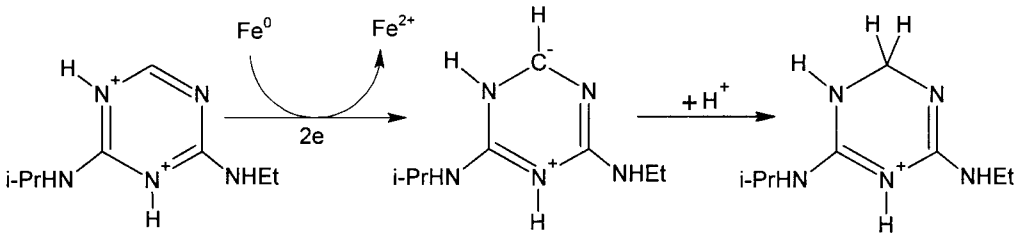


FIGURE 49. The possible second 2-electron reduction of triazine ring.

Obviously, product IX lacks of aromaticity and thus is not as stable as its parent s-triazine herbicide. Possibly the ring cleavage occurrs soon afterwards.

Although such a process (the second 2-electron reduction) is not directly observed by GC/MS analysis, it is very likely to occur. The GC/MS analysis in our experiment used a C-18 Solid Phase Extraction Cartridge to trap the reduction product. It might miss the molecules if they were very polar or small. Actually, dechlorinated atrazine (VI) disappears very quickly in the reduction (in the presence of Fe^0), which might account for this further reduction and ring cleavage.

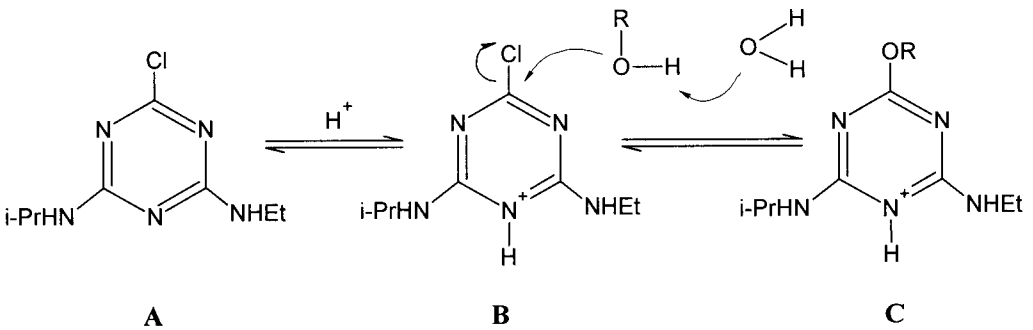
4.4.2. Hydroxyl Atrazine and Other Derivatives

The formation of methoxyl atrazine could be explained by 2 possible reactions. One was due to use of methanol in GC-MS as solvent. At the high temperature (~270°C) inside the liner of the GC system, a methoxyl group could directly replace the chlorine. This result was confirmed by injecting methanol solution of atrazine into GC-MS. The other way is the nucleophilic substitution in an acidic environment. Like hydroxyl group in water, the methoxyl group of methanol is a weak nucleophile. In normal conditions (neutral pH), the replacement of chlorine of atrazine by methoxyl group is slow. However, once the triazine ring is protonated, the methoxyl group can readily replace the chlorine (S_N2) since this positive triazine ring is susceptible even to weak nucleophile attack. A very poor nucleophile like iso-propanol (used to improve the solubility of atrazine in water) could replace the chlorine of atrazine in protonated form. These substituted products could

be observed by GC-MS analysis (Figure 36).

Similarly, hydroxyatrazine might also be formed this way. Unfortunately, it could not be analyzed by GC-MS directly due to its higher polarity and lower vapor pressure. Normally, in our test, the HPLC chromatogram of atrazine degradation solution didn't show a hydroxyatrazine peak since the UV detector was set at 220nm, which was not proper for hydroxyatrazine analysis (Figure 38). Also, it was supposed to be a minor product and thus a weak signal. However, clear evidence of alkoxyatrazine (especially, isopropoxyatrazine) existence could be used as an indication of hydoxyatrazine existence since both are similar weak nucleophiles. The mechanism is shown in Figure 50.

The easy appearance of methoxy or iso-propoxyatrazine associated with the Fe^0 degradation process of this experiment indicates that the substitution of chlorine could proceed in acidic solution if there were some proper nucleophiles, like hydroxy group (of water), which could form a more stable triazine compound.



R= H, CH_3O, *i*-PrO or alkoxyl group

FIGURE 50. Mechanism of the formation of hydroxyl atrazine and alkoxyl atrazine.

It was further confirmed by LC/MS Q1 scan. At pH=2, hydroxy-substituted product of atrazine was observed after one week, and its content was increasing (Figure 28, 29, 30). The result was estimated by the area ratio of hydroxy atrazine vs atrazine. Hydroxy product in the degradation process of atrazine might be regarded as a desired degradation product since it doesn't contain aromatic halogen, and thus is probably less toxic.

However, compared with the major degradant in Fe^0-promoted reduction, hydroxyl or alkoxyl products constituted only a very minor part. It might be further reduced by Fe^0. For instance, Singh *et al.*(1998) reported a similar degradation speed for both atrazine and hydroxylatrazine in the presence of Fe^0.

In the Fe^0-acid process, since the major degradant observed contains no aromatic chlorine, it should not be treated as a new pollutant; another advantage of Fe^0-acid process is the possible ring cleavage product(s), which may be regarded as a complete degradation. So far, no detailed toxicity of hydroxyl atrazine, alkoxyatrazine and dechlorinated atrazine has been reported.

5. CONCLUSIONS

(1) There have been several atrazine degradation ways explored. Among them, the degradation by zero valent iron appears to be a cheap, simple and practical method. And it can be regarded as a complete degradation. It is carried out simply in deoxygenated acidic solution with Fe^0, and no other necessary facilities.

(2) Transfer of this Fe^0-acid degradation process into a column provides a pilot study of a practical application in soil at a pollutant site. In this study, a maximum of 63.1% of degradation in the column was achieved and the minimum length of the column of 7.8 cm was necessary. It should be indicated that, for analytical convenience, this study dealt with concentrated atrazine solution, at ppm level, while in the actual contaminated water, the atrazine concentration is normally at ppb level! So a more favorable degradation result is expected for lower atrazine concentration (ppb), which is more likely the case of natural environment.

(3) pH of the reaction solution was very important to the degradation rate of atrazine. For the column reaction, a low initial pH played a key role for the overall result. It is possible that in certain soils, the natural existence of humic and fulvic acids might provide a sufficient acidity to the practical application of this method.

(4) Bromide, as a tracer, is simple and convenient to use in this research, which provides a reliable way to understand the diffusion characteristic of the column.

(5) The intermediate degradant, dechlorinated atrazine, contains no aryl halogen and should be environmentally less harmful. The "endogenous" degradant, hydroxyl atrazine has no known harm compared with atrazine, since its aryl chlorine is replaced.

(6) The dechlorination approach with Fe^0 could be applied to other triazine herbicides as well as organic pollutants that contain chlorine. This approach is potential for more environmental remediation.

(7) To the consideration to environmental remediation, it is helpful to combine more advantaged processes together. Atrazine degradation could be facilitated by acidic condition and UV light. It is possible that an improved way of degradation with zero valent Fe could combine these processes.

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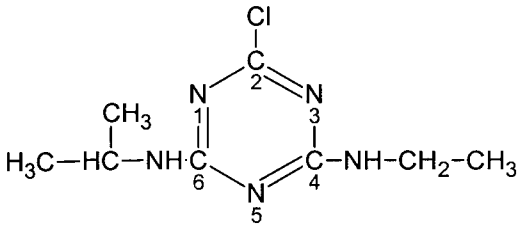
7. APPENDIX

TRIAZINE HERBICIDES*

The chemical structures of the diamino-s-triazine herbicides are centered on a common six-membered ring structure composed of three nitrogen and three carbon atoms arranged symmetrically (in this case, alternately) about the ring, with an amino (NH_2) group bonded to the carbon atoms at the 4- and 6-positions of the ring, as shown below:



A six-membered ring structure with two or more nitrogen groups in the ring is call **"azine"**. When there are three nitrogen atoms arranged symmetrically in the ringstructure, it is called **"s-triazine"**.

The triazine herbicides are divided into three major groups depending on the type of substitution at the R1 position on the ring. The chlorotriazines are chlorinated. Their common names end in zine; for example, simazine, atrazine, cyanazine, and propazine. The methylthio-triazines are substituted with a -SCH_3 group and common names end in -tryn (ametryn, terbutryn, prometryn). The methoxytriazines have an -OCH_3 group at R1 and end in -ton (prometon).

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* Abridged from: 1. http://courses.cropsci.ncsu.edu/cs414/CH_8.PDF *(accessed on 01May04)*
2. http://www.alanwood.net/pesticides/class_pesticides.html *(accessed on 15May04)*

Several important properties are determined by the R1 substitution. As a rule of thumb, the methoxytriazines are more mobile, more persistent, and less selective than members of the other two groups.

The triazines are potent photosynthetic inhibitors that are activated by light, causing chlorosis and desiccation of green tissues. They move apoplastically, whether taken in through the shoots or roots. When soil applied, triazines are readily taken up by the roots of seedlings and move into the emerging foliage. Seedlings typically emerge from the soil and grow until they exhaust the food stored in the cotyledons. They then become chlorotic, desiccate, and die back.

Hexazinone is a symmetrical triazine herbicide, but it is not a diamino-s-triazine. Metribuzin is a triazine herbicide, but its chemical structure is asymmetrical. The characteristics of these two herbicides are similar to those of the diamino-striazine herbicides.

Members include:

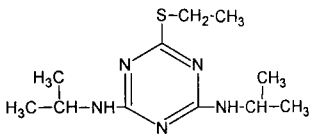
Triazine herbicides

dipropetryn
triaziflam
trihydroxytriazine

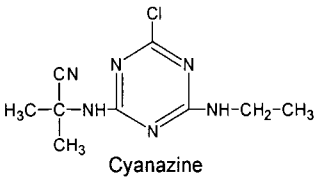
- **chlorotriazine herbicides**

  atrazine
  chlorazine
  cyanazine
  cyprazine
  eglinazine
  ipazine
  mesoprazine
  procyazine

Some Structures

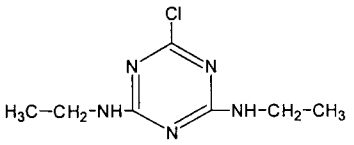


Dipropetryn



Cyanazine

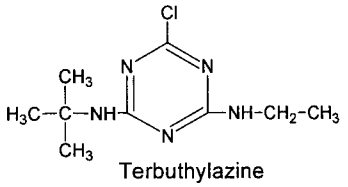
proglinazine
propazine
sebuthylazine
simazine
terbuthylazine
trietazine



Simazine

- **methoxytriazine herbicides**

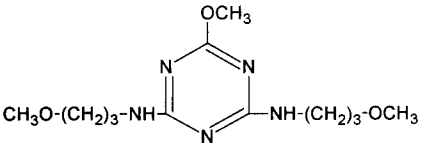
atraton
methometon
prometon
secbumeton
simeton
terbumeton



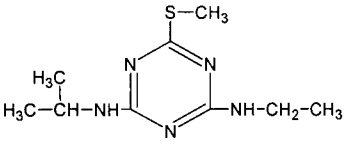
Terbuthylazine

- **methylthiotriazine herbicides**

ametryn
aziprotryne
cyanatryn
desmetryn
dimethametryn
methoprotryne
prometryn
simetryn
terbutryn



Methometon



Ametryn

SELECTIVITY

Crop selectivity to these herbicides is achieved by rapid detoxification in tolerant species, the inability of sensitive species to detoxify them, and by the proper placement of the herbicide relative to the root zone of the crop plants.

Common Characteristics

1. The triazine herbicides are readily absorbed by both the roots and foliage. The addition of a suitable surfactant to the spray mixture greatly enhances foliar wetting and herbicide absorption. Translocation is apoplastic.

2. Soil-applied triazine herbicides do not control established annual or perennial weeds or deep-rooted perennials when applied at the dosages recommended for selective weed control in croplands.

3. The triazine herbicides are readily absorbed to soil colloids, and they resist leaching. However, leaching can occur, depending on soil texture, the volume of water percolating through the soil, and the herbicides involved.

4. The soil persistence of the triazine herbicides is about 1 month to more than 12 months, depending on the herbicide and application rate and environmental factors such as rainfall, soil organic matter, soil pH, and soil temperature. Soil persistence is longer under arid conditions than under humid ones.

5. Following many years of continuous use of the triazine herbicides (and other herbicides with the same mode-of-action), resistant weed biotypes of some species that are not controlled by these herbicides have developed.

6. Simazine has little or no foliar activity, and it is used only as a PRE herbicide.

7. With the exception of simazine, each of the triazine herbicides is foliarabsorbed.

8. Prometon is used only as a nonselective herbicide for general weed control in noncrop areas, **it generally controls all plant growth for a year or more**.

9. Chemical hydrolysis is the primary means by which atrazine, cyanazine, and simazine are detoxified in soils.

10. Microbial degradation is the primary mechanism by which ametryn, hexazinone, metribuzin, prometon, and prometryn are lost from the soil. Degradation occurs fastest under aerobic conditions and comparatively high temperatures.